図 本館

STUDIES ON ATOMIC SPECTROSCOPY FOR TRACE ANALYSIS

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PREFACE

Twelve years ago, the author started a study on analytical atomic emission spectroscopy using a capacitively coupled microwave plasma as the exciting source, under the late Professor Tsugio Takeuchi's pertinent direction.

In the experimental study on the characteristics of the plasma, he had encountered notable inter-element effects. In order to analyze the effects systematically, a certain method was necessary. From the necessity was developed such a method that the excitation temperatures of atoms and ions, and the degree of ionization were determined from the intensities of atomic and ionic multi-lines, with equations based on the Boltzmann's law. The method named MULTI-LINE METHOD has been one of the main subjects of the author's research.

During the author's tenure of office at Naka Works, Hitachi Co. Ltd., he had a chance to come into contact with atomic magneto-optics owing to Dr. Hideaki Koizumi, Dr. Kazuo Yasuda and Professor Tetsuo Hadeishi. Appointed a staff at Nagoya University owing to Professor Shin Tsuge and the late Professor Tsugio Takeuchi, the author reopened the study on the MULTI-LINE METHOD and concurrently started a study on application of the atomic Faraday effect to analytical spectroscopy–ATOMIC MAGNETO-OPTICAL ROTATION SPECTROSCOPY. The latter method is mainly associated with the removal of background signals caused by non-atomic species evolving in direct atomization of samples.

Thus, since then, the developments of analytical atomic spectroscopic methods to overcome the problems associated with background signals and interferences have been the main subjects of the author's research. This dissertation is written as a conclusion of these studies and also to give a motive power for the author's future work.

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Kuniyuki Kitagawa

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ABSTRACT

In this dissertation entitled "STUDIES ON ATOMIC SPECTROSCOPY FOR TRACE ANALYSIS" the author describes two novel atomic spectroscopic methods for direct analysis of trace amounts of elements; "ATOMIC MAGNETO-OPTICAL ROTATION SPECTROSCOPY" using the atomic Faraday effect and "MULTI-LINE METHOD" in which atomic, ionic and molecular lines are compared.

The former has such features as high recovery of light source energy and capability to remove scattering light in addition to those of atomic fluorescence spectroscopy, and is therefore suitable for trace analysis of samples in complex matrix by direct atomization. The latter is developed for spectroscopic correction of interferences caused in diverse types of atomizer and exciting sources for analytical atomic spectroscopy, and also useful for the elucidation of interference mechanisms.

In INTRODUCTION is described an author's view on analytical chemistry and analytical atomic spectroscopy, involving historical changes, current status and some future trends. This is intended to make clear his motive to adopting the two methods as the main subjects.

In chapter 1 are described the history, theory, instrumentation, experimental aspects and some application of atomic magneto-optical rotation spectroscopy.

In chapter 2 are described those of the multi-line method.

In SUMMARY are described the problems associated with the two methods and possible ways to overcome them.

In order to represent the nuance of the author's viewpoint properly, the texts in INTRODUCTION and SUMMARY are written in his mother tongue, or Japanese.

序　　論
(INTRODUCTION)

はじめに (Prologue)

本論文において著者は元素の痕跡分析のための二つの新しい原子分光学的方法について述べる。その中で，それらの方法の基本的な分光学的特徴，関係する理論，装置化についての問題，若干の応用などについても論ずる。

二つの方法のうちの一つは，原子ファラデー効果を利用した「原子磁気旋光分光法」であり，元素の痕跡量の直接分析に適している。原子けい光分光分析では複雑で多量なマトリックスを含む試料を分析する際にバックグラウンド散乱が問題となるが，本法にはバックグラウンド散乱を除去できるという特長がある。また前方で光を検出するため光源光エネルギーの回収率が高いなどの特長もある。

二つの方法のうちのもう一つは「多線法」であり，これは，原子吸光分光分析や原子発光分光分析において見られる試料マトリックスによる干渉を解析したり補正したりするのに有用である。

上記のように著者は原子分光法による元素の痕跡分析における種々の問題のうち，二つの問題，即ち試料マトリックスによる見かけの光信号「バックグラウンド信号」，および試料マトリックスにより光信号強度が変化してしまう「干渉」の問題に焦点を絞り，これらを軽減させる方法を本論文の主題としている。これらの問題は特に生体試料などの複雑かつ多量のマトリックスを含む試料を直接分析する際に深刻となる。

本論文の詳しい記述をする前に，著者がなぜこれらの問題を重要視するに至ったかを説明するためには，著者の分析化学（特に分析化学発祥の古から続いている無機分析）について感ずる所をある程度一般的に述べた方が良いと思う。分析化学の歴史的背景，関係するいくつかの因子，無機分析に使われる原子分光法以外の種々の方法の特徴，現在における無機分析に対する社会的要求などを述べた後，それらに相関付けながら原子分光分析の現状を大ざっぱに解析し，それとの関連で主題の位置付けをする。その中には，現状解析から著者が感じた原子分光分析の将来的な方向もいくらか含まれている。

1. 著者が悩み思う分析化学 (Analtytical chemistry—What the author is afflicted with)

分析化学と他分野 (Analytical chemistry and other fields)

「分析化学」というものを適切に定義して他の分野の科学者にうまく説明することはなかなかむつかしいと思われる。特に「『分析化学』は何を明らかにしようとする科学か」という立場で聞かれた時，著者自身，しばしば悩む。これは恐らく，分析化学が現在においては非常に多種の分野に複雑に関係しているためだろうと思う。それでも，仮に，次のように答えたいと思う。分析化学とは「定性的，定量的に分析物の特徴についての情報を与えるための科学と技術の合同体」であると。他の人も種々の定義をしているが〔Ｉ１～Ｉ３〕，一応著者はこのように定義しておいてもう少し

感じるところを述べてみよう。

現在においては，多種の科学者や技術者が分析化学に貢献している。例えば，分析化学的方法のうち磁気共鳴分光法，質量分析法，原子分光法，メスバウァー分光法などの多くの分光法の理論的な面では量子力学や電磁気学の展開を通して物理学者が非常に多大な（ほとんどと言ってもよいかもしれない）寄与をしてきている。またこれらの方法の装置化の過程では光電子増倍管などの検出器またはセンサー工学やその信号処理に必要な電子工学に携わる技術者の貢献も多大である。また一方では，分析化学的方法を用いて日常分析を行っている科学者や技術者は，ある特定な分析対象物に関する分析化学的方法の最適な使い方（ソフトウェアー）については卓越しているかもしれない。例えば，有機合成化学者は合成物の同定を行うために赤外分光計，核磁気共鳴分光器，紫外分光計，元素分析装置などを使いこなす中で，これらの方法の改良，発展にソフトウェアー的な立場から大きな寄与をしているといえる。では一体，分析化学者はどのように分析化学に関与しているのであろうか。

分析化学者とは？ (What is analytical chemist?)

このことを論ずるためには，分析化学者と他分野の科学者の違いを考える必要があると思われる。両者をはっきりと区別するのは非常にむつかしいが，著者は一応，次のように考える。例えば物理学者や，もっと分析化学に近いところでは物理化学者は分析化学的方法を開発し，使うにしても，彼らの最終目的は現象や物性そのものを明らかにすることであって，その目的に合わせて分析化学的方法を改良する。それに対し分析化学者は広い応用分野における多様なニーズに適合できるように分析方法を改良して行く。時には，分析化学者は「どうしたらこの方法を市販品とし具体化して普及できるだろうか」というような極めて実用的な事に思いをめぐらす。そのために利用できる種々の原理や技術はできる限り使ってみようと思う。したがって関係する分野は時として非常に広くなる。だから分析化学者は割合にどの分野の人とも話ができるように思える。しかし，利用している分野の研究そのものをしているわけではないので，即ちその道の専門家ではないので必ずしも対等にはその分野の研究そのものを話せないと思われる。したがって，悪くみると分析化学者は，物理学者と話すときは化学を，医者と話すときは電気や物理の話をする嫌いを持つと言えなくもない。このような複雑で多面的な分析化学者の性質は他の分野（特に純粋科学）に携っている人々には非常に理解し難いものかもしれない。しかし著者はあえてそれが，最初に著者が仮に定義した分析化学の目的を達成するためには良く適合しているものだと思いたい。

この分析化学者の多面的な性質がどのように育てられたかを理解するためには分析化学の歴史を振り返ってみる必要があろう。

2. 分析化学の生い立ち (Historical aspect of analytical chemistry)

分析化学的概念の発生 (Conceptual genesis of analytical chemistry)

組成の違いによる物の違いを知る必要性は文明が現れた古代においても人々は知らず知らずの内

に身に付けていたのかもしれない。例えば古代中国人や古代エジプト人は防腐剤として水銀化合物や樹脂を用いたが，そのためには物質の同定は欠くべからざることであったろう。

物質の組成についての観念論はアリストテレスの四元説にみられるように既に紀元前三〜四百年頃から存在していた。しかし，もっと実践的な化学（chemistry はエジプト学を意味するとも言われている。）はエジプトからサラセン文明に移入され7〜10世紀頃に錬金術となり13〜17世紀頃，ヨーロッパで盛んとなった。この時期においても金属の同定のため灰吹き法という分析方法があった〔Ⅰ5〕。錬金術では他の金属から金を造ることができなかったが，関連技術の発達により，鉱酸，金属酸化物，塩類などの無機化合物（エーテル，アルコール，エステルなどの簡単な有機化合物も）に関する実験技術は，その頃までに貯えられていた。しかし，系統的な学問にまでは達していなかった。

17世紀においてこの状態に光を与えたのはイギリスの Boyle で，「懐疑の化学者（Skeptical chymist）」という著書の中で化学の法則は根拠のない仮定から導き出されるものでなく，多数の実験結果を総合して帰納的に結論すべきことを主張している〔Ⅰ99，Ⅰ100〕。化学の体系化を指摘しているわけだが，この著書の中で注目すべき点がもう一つある。それは，既にこの著書の中で「分析化学に関連する言葉（chemical analysis，analytical，analyzed，analyzing，analyzer ）が出現していることである。化学の学問としての体系化の最初の段階で分析化学は同時に含まれていたのである。Boyle はその頃，既に酸－塩基によって色が変化する物質，即ち指示薬の研究をしており，比重の測定法の系統化と合わせて溶液分析の下地を作った。

彼の仕事で注目したいのは，彼は上記のような純粋科学的な追究だけでなく，社会的要求に応じた実際的な方法に関係した仕事をもしていることである。当時の海軍が必要としていた海水から真水を作ることを研究して王に結果を披露したり，それから発展して，鉱水の分析のための約30の検査項目を作ったりした。

著者は冒頭で分析化学者の性質について触れたが，Boyle のこの学術的な面と実際的な面が明確に分離されてなくて同時に持ち合わせるという性質（もっともこれは当時の未分化の学問体系では普通なのかもしれないが）は今日の分析化学者に，根強く継承されているのかもしれない。これを一応，「分析化学魂」と以後，呼ぶことにしよう。

Boyle 以後，Stahl，Scheele，Priestley／Cavendish，Lavoisier，Proust，Dalton，Gay-Lussac，Avogadro 等の有名な化学者により化学の体系化が進んだ。それに従って，分析化学もしだいに体系化，定量化されつつあった。また，1760年に端を発した産業革命によって化学工業が盛んになるにつれて，材料，製品の品質検査が必要となり，分析化学は社会的要求によって進められることも多くなった。このような背景から19世紀中頃までには容量分析の原形が既に用いられていた。このように，Boyle 以後の18〜19世紀のいわば化学の幼年期の頃においても分析化学は社会的要求に近いところで進化していた。このことは，Boyle の頃にもみられた学術的および実際的の両面を持ち合わせる性格を，20世紀に入って学問がしだいに分化する中でも分析化学が失わない一因

になっているかもしれない。

物理化学との結合 (Connection with physical chemistry)

20世紀に入って物理化学の発達は容量分析法や重量分析法による無機分析の理論的な裏付けを促した[I 4]。これらの成果は現在，学生の分析化学実験の指導書の中に盛り込まれている。一方，電磁気学，量子力学などの物理学の発展に伴い，いくつかの原理が分析化学に入りつつあった。第二次大戦が始まるまでに磁気共鳴や質量分析法などの機器分析法に関する理論の一部は既に展開されていた。この20世紀前半の時期は，仮に19世紀までの分析化学を第一期分析化学とすると，第二期と呼んでも良いだろう。

機器分析の発達 (Developments in instrumental analysis)

第二次大戦中，主に軍事目的のために発達した技術により，大戦後，それまでに積み重ねられていた分析化学に関する原理は急速に具現化されるようになった。その後，検出素子や電子工学の急速な発達に伴い，機器分析法は益々，複雑で高度なものになりつつある。20世紀後半を分析化学の第三期とみてもよいだろう。

さて，第三期に入ってから，分析化学に関係する分野は益々広がり複雑化してきている。特に，機器分析においては物理や電子工学の占める割合は現在ではかなり多い。このような状況の中ではたして分析化学者は存在できるのであろうか。17~19世紀に育れた分析化学魂は継承されていくのだろうか。この種の悩みは物理学的色合いの濃い分光分析に携わる分析化学者ではよけいに強いかもしれない。この問題をもう少し深く追求するために以下に現在の分析化学の状況や関係する因子を考えながら解析してみよう。

3. 現在の分析化学の状況 (Current status of analytical chemistry)

分析化学の三要素 (Three components in analytical chemistry)

分析化学者は時々，「理論的方向に行くべきか，一応それは置いておいて，経験的に追究することにしようか」と迷うことがある。また，「物理的な方法をとる方が適切なのか，化学的方法の方が良いのか」と迷う場合もある。分析化学者のこの種の迷いや悩みは主に，分析化学的方法の研究における，分析化学を構成している科学的ベースの選択に起因していると思われる。

表１－１に，分析化学に関連する科学的分野を大まかに分類したものを示す。表の上ほど理論的色彩が濃い分野であり，下のものほど経験的色彩が濃い分野である。より経験的な分野の研究者はより理論的な分野から必要な理論的ベースを引き出そうとするし，逆に理論的分野の研究者は打ち立てた理論の実証のために経験的な分野における実験を必要とする場合がしばしば生ずる。このような分野の交叉において時々，科学者は交叉域のどの辺に力点を置いて研究の方向付けをするかを迷うことがある。この種の交叉は，冒頭に述べた分析化学の目的を果すためには，広く，多岐，多様に渡る。このことが，分析化学者に科学的ベースを選択する上で，純粋科学に関係する人々より多くて複雑な迷いを与えるのであろう。

Table 1-1 Scientific bases of analytical chemistry

Theoretical/pure	Mathematics
↑	(Astronomy)
	Physics
	Chemical physics
	Physical chemistry
	Chemistry — Analytical chemistry / Synthetic chemistry
↓	Biochemistry
	Biology
Empirical/applied	Medicine

分析化学者はまた，分析化学的方法を研究する際，もっと深刻な悩みをしばしば抱える。それは，分析化学的方法の原理や理論に関することを主に追究するか，その原理を具体化するために必要な装置開発（ハードウェアー，技術）に力点を置くか，一応完成している方法，装置を用い応用を行うのに必要な手順を確立する（ソフトウェア）ことに重点を置くのか，ということである。これらはいずれも分析化学を成す要素であって必要不可欠なものだと思われる。図1に著者なりに考えた分析化学の三要素を簡単に示した。分析化学は科学的ベース（種々の分野の原理，理論），技術（ハードウェアー），応用（ソフトウェアー，社会的要求）からなっている。

Fig. 1 Triangle of analytical chemistry

三要素の均衡のむつかしさ (Difficulty in balancing the three components)

ところが，この三つの要素のどれをとっても分析化学者は，最初からはその専門家ではない場合が多い。したがって，核磁気共鳴分光法の分野のように物理学者や電子工学者が活躍すると，一面で

は化学に基盤を置く分析化学者はどうしたらよいか悩むかもしれない。Laitinen は[I4]，このことを良く言い表わしている言葉として1962年の Fisher Award の受賞挨拶の中で Liebhansky が言ったことばを挙げている。「分析化学から化学が出て行きつつある。」しかし，Laitinen は，歴史的に伝承されている分析化学魂が必要であることを次のように言い表わしている[I4]。「分析化学魂が現実の世では必要であることは，『物理学者は純粋な系を扱いたがる，というのは彼らは時々，複雑な系においてマトリックス効果に悩まされるからだ』ということを考えるとよくわかる。」著者に関係があるものとしては原子発光分光分析用のプラズマ励起源がこの例にあたる。核融合開発においてプラズマ理論はかなり展開されているが，これはあくまで，一成分の純ガスについてのもので，複雑なマトリックスを含む生体試料などがプラズマに入ったら，およそ適用はむつかしいであろう。

しかし，それでは理論は物理，物理化学者らに，電子回路は電子技術者に，実際の応用は例えば臨床分析者に任せておけばよいのだろうか。著者は，分析化学者は最大限，三つの要素を常に滋養としてとり入れる努力をする必要があると思う。分析化学魂は必要不可欠であるが，それを具体的な方法，装置とするためには，苦しいが上記の事は避けて通ることはできないと思われる。そうすることにより例えば物理学者との会話がよりし易くなり分析化学的手法へ応用できそうな原理を探し出す機会が増加するであろう。逆に物理学では扱わないような複雑な系での発見も物理学にフィードバックし易くなる。また，電子技術者との会話が十分に行えれば分析化学的方法を装置化する際，目的によく合った設計ができ，ブラックボックスが排除されるために，真の分析値と表示値のくいちがいを最小限にできる。応用分野の人々と話すことは分析化学に関する社会的要求を知る上では欠かせない。その時も，分析化学者がその分野のより専門的な事を知っていることは，要求をより十分に理解する上で重要であると思われる。

時として，もともとは純粋科学者であって分析化学者ではなかった人が分析化学魂を感じ取り，分析化学者になる場合がある。このことは，図1の三要素を結ぶ三角形の一辺に摂動を与え（その人は一要素の専門家であるから）それが三角形全体の膨張に寄与することもある。

方法開発の時間的推移 (Temporal change in development of a method)

こうして分析化学はしだいに進展するが，その中で分析化学者はある時点，時点において，三要素の均衡を図ることに苦悩する。このことは一つの分析化学的方法を開発，装置化，応用するとい

Table 1-2 Time flow chart of the progress of an instrumental analytical method

Mechanism study (Feedback concept)

1. Concept, theoretical basis or principle
2. Experimental verification of the concept applicability
3. Instrumental design and hardware (technological) optimization
4. Standardization and software (procedure) optimization in practical applications

う時間的推移の中でも端的に見られる。以下にそれを示す。

Barnesは原子発光分光分析用の励起源である高周波誘導プラズマについての総評の中で〔I 10〕機器分析法の進歩において，概念，実験的確認，装置開発，原理および機構解明，標準化，衰退という六つの段階があることを示している。これを著者が四段階に単純化し，フィードバックの経路を付加したものを表１－２に示す。

発想，原理，理論の段階 (Stage of concept, principle and theory)

第一段階は発想の段階で，分析化学者はこの段階で一つの分析化学的方法についての基本的な考えを思いつく。発想の動機にも図１で示した三要素の重みの具合で次の三つが考えられる。一つは現象の発見や理論の研究の中でそれらが分析化学的方法に応用できることに気が付く場合である。例としては磁気共鳴分光法がその一つで，量子力学や電磁気学の興味からいろいろなモードの二重共鳴法や時分割法，データ処理法が生み出された。二つ目は，工学（技術）的な興味からある方法を思いつく場合で，例えばホトダイオードアレイ検出器やシリコンインテンシファイドターゲットなどのイメージセンサーが十分な性能を持つようになってからいろいろな多元素同時分光システムが考案された。医用工学（医用電子工学）の分野でも，電子計算機が発達したため断層写真法が実用装置として具現化された。核磁気共鳴分光法でフーリエ変換法が実用的になる裏では電子計算機の寄与は大なるものがある。三つ目の場合は応用分野における社会的要求から動機が生ずる場合である。この場合，分析化学者はその目的を果たすために必要な原理や理論，工学（技術）を探す。例えば，環境分析の応用分野では，海水や河川水中の ppt～sub ppbの濃度の水銀を定量したいという要求は続いている。それに対応できる方法が十分に確立されていないことも手伝って，原子分光分析の分野では現在，多くの研究者がこの問題を取り扱っている。

以上の三つの場合は完全に独立しているわけではなく，複雑に入り組んでいる。分析化学者はこのような形で第一段階として，分析化学的方法に対する動機を持つであろう。

原理，理論の実験的実証の段階 (Stage of experimental verification of the principle and theory)

第二段階は第一段階で出された原理や理論が感度，精度，選択性などの分析化学的パラメータのうち要求されているものの条件を満足するような方法として具現化できるかどうかを実験的に確認する段階である。この段階で分析化学者は，大まかな実験をすればよいか，精密な条件を設定する方がよいか迷うことが時々あるが，それも分析化学的パラメーターに沿って合理的に判断する必要がある。また，この段階で使われている原理や理論が不適当だと判明したときはもう一度，第一段階に戻って，考え直さなくてはならない。（フィードバック）

装置化の段階 (Stage of instrumentation)

第三段階は第二段階で確認した原理や理論を応用した具体的な装置を作る段階である。この段階ではいろいろな工学（技術）が使われるが，現在の機器分析の概念に最も近いのは「計測工学」であろう。計測工学には，対象物が有している物理量をいかにして人間や電子計算機が受け入れられる量（典型的にはメーターに表示された電流や電圧）に変換するかという目的がある。計測工学は，

主にセンサー（センシング）工学と信号処理工学という二つの部分からなる。前者の目的は，いかにして目的とする物理量を（選択的に）対象物から引き出すかということである。これは，広く解釈すれば分析化学の目的と酷似しているが，実際には，何のためにどのようにそれを使うかというようなソフトウェアーを含めずに装置（ハードウェアー）そのものに限定した狭義の解釈をした方が混乱しないと思う。しかし，センサー工学は機器分析の重要な部分の一つに違いない。

信号処理（電子回路，電子計算機）(Signal processing—electronic circuit and computer)

後者の信号処理工学も機器分析に不可欠なものである。センサーからの信号を処理し人間がより理解し易い形にする。また，複数の情報を合わせて処理することにより，生の情報のみでは分かりにくかった情報が与えられることもある。前に掲げたフーリエ変換核磁気共鳴分光法や電子計算機断層写真法などはその典型であろう。本論文の主題の一つの多線法もこれに類する。これらの複雑な信号処理にとって，最近になって急速に発展した電子計算機は必需品となってきた。ところが，分析化学者にとっては，電子計算機はかなり敷居の高いもののように感じられる。例えば，Willis は「古きスペクトロスコピストはいずこにいるのか」という所感の中で，古いスペクトロスコピストはマイクロコンピュータという新しい道具の出現に，かなり困惑し，なかなかそれを受け入れることができないと述べている〔I 11〕。この原因の一つには，電子計算機を分析機器に組み合わせる際のハードウェアーの複雑さと，それを使いこなすためのソフトウェアーの開発において使われるプログラム言語がまだまだ人間の感覚になじまないことが挙げられる〔I 101〕。

しかし，信号処理回路の機能が不適当であると，表示装置からは正しい情報を得ることができなくなること，また，信号処理以外にも，分析装置を制御（例：温度制御などの条件制御やオートサンプラーなどの自動装置の制御）する上で不可欠なこと〔I 101〕などを考えると，コンピュータを含めた電子回路に分析化学者が馴染んでいることは正しい分析結果を与える方法を開発する上で非常に大切な事であると思う。

応用の段階 (Stage of application)

第四段階は，第三段階で装置として具現化された方法を実際の分析に応用し，試料採取の方法から化学的前処理などの過程を含むソフトウェアーを確立し，その方法を用いた分析手順の最適化を図り標準化する段階である。方法の評価には他の方法，異なった試料形態，研究室間でのクロスチェックなども重要である。この段階でも分析化学者は，開発した方法が広い応用分野にわたってユニバーサルなものにするためのチェックを行うか，ある限定された範囲の分野の要求を満たすものにするか，という二つの方向があることを感ずることがある。応用分野で，ある分析目的を持ってそれを専門に研究している人（例えば公衆衛生を研究目的として人血中の鉛を専門に行っている人）は後者の立場を取るであろうが，分析化学者は最初からはその分野の専門家とは限らないため応用分野からの要求があった場合，上記二つの方向の選択に悩むことが時々ある。

フィードバックの段階 (Stage of feedback)

さて，第四段階における方法の標準化のためのチェックの中で，種々の不都合な問題が生じてく

る。これを解決するためにはその原因を解明すること（メカニズムリサーチ）が重要である。（このことについては序論の最後でも本論文の主題に関して述べる。）原因を知った上で，第二，第三，場合によっては第一段階に戻る必要がある。（表１－２参照）

方法の改良としては，一つの方法の改良だけでなく，二つあるいはそれ以上の数の方法を結びつけて，それぞれの方法の欠点を相補うことによって全体としてさらに優れた方法とすることも有効である。このような「方法の結合」の典型の一例としては，ガスクロマトグラフィーと質量分析法の結合が挙げられよう。

このようにして，方法の最適化が進むが，しだいにそれもある限界に達することがある。このような場合には表１－２に示すように，もう一度，第一段階に戻って原理的なところから発想の転換を図る必要がある。

以上に，一つの分析化学的方法が装置をも含めて確立されて行く流れと，その中においても分析化学者にはいろいろな悩みや迷いがあることをみてきたが，では一体，その複雑な悩みや迷いを性として持ちながらも分析化学者が探し求める目標は何であろうか。これも複雑，多様でそのすべてを網羅し，明確に分類することは困難であるが以下で著者なりに考えてみる。

4. 分析化学者は何を追究するのか――その因子(What analytical chemists pursue—its parameters)

理想的な分析法 (Utopian analytical methods)

冒頭で分析化学の定義を仮にした。分析化学者は時としてこの定義を完全に満足するような分析法や，分析装置を夢見る。例えば，ある分析対象物に向けるだけで，それについての任意の情報が得られるような万年筆のようなもの。このようないわば分析化学的ユートピアに向かうという精神とそのための発想の転換は重要ではあるが，熱力学の法則に逆らう，いわゆる「マックスウェルの悪魔」のようなものがいない限り，ユートピアに到達するのはほとんど不可能であろう。したがって，分析化学の目的を因子にわけ，そのうち限定した数の因子で与えられる条件を満足する方法や装置を開発するのが現実的である。

分析化学の必要因子 (Essential parameters in analytical chemistry)

表１－３に大まかに考えられる因子を掲げる。上で述べたような因子限定の方法にも限定の程度で大まかに二つある。一つは，限定の範囲が比較的広いもので，ある分析化学的方法や装置を種々の応用分野に広く適用できる汎用性のものとするやり方である。このやり方は，表１－２の第一段階において，分析化学的方法の発想が理論的興味や工学的興味から出てきているものの場合に比較的多いと思われる。もう一つの限定の方法は，限定の範囲を比較的狭くある特定の因子に力点を置くやり方である。このやり方は，分析化学的方法の発想が応用分野のある特定な要求を源に生じたものの場合に比較的多いと思われる。後者の場合について，応用分野と関係づけて簡単に考えてみる。

Table 1-3 Parameters involved in analytical chemistry

- Target (single component) analysis / Multi-component analysis
- Identification/qualitative / Determination/quantitative — Characterization
- Bulk / Image (distribution/localization)
- Destructive / Non-destructive — In-situ, In-vivo — In touch / Remote sensing
- Absolute / Calibration — Direct / Indirect — Separative / Non-separative

Sensitivity/trace, ultra-trace/counting
Selectivity/specificity/high resolution
Precision
Accuracy
Wide adaptability for sample form/small sample size
Rapidness
Stability/reliability

Academic fit/particular performance regardless of cost
Commercial fit/high performance to cost ratio,
small amounts and low toxicity of reagents and radiation,
ease to operate,
low energy consumption,
beautiful design,
social needs etc.

Table 1-4 Application fields of analytical chemistry

Pure Science	Geochemical (luna stones etc.) Physical Physical chemistry
Industrial	Coatings (IC, films etc.) Fuels/oils/petroleum/ores Metallurgy (ferrous, non-ferrous) Products (Rubber, polymers, fertilizers etc.)
Environmental	Air pollution (particulates, gas) Water analysis (floating matters, water) Pesticide residue
Biomedical	Pharmaceuticals/drugs Fertilizers Foods Clinical and medical chemistry (biological tissues/fluids)

感度，迅速性 (Sensitivity, Rapidness)

表１－４に分析化学が関係する応用分野を大まかに分類したものを掲げる。それぞれの応用分野に特有な試料の分析においては，表１－３の中のある特定な因子が特に重要であると考えられるような場合がある。例えば，臨床医学における血液や薬の中の元素の分析においてはまだまだ感度が不足している。実際にアルカリ金属，アルカリ土類元素などの主成分は別として，鉛以外の微量元素の体液濃度はかなり低い（数 ppb ～ppb 以下）。また，生体試料の複雑なマトリックスを除くための前処理によって希釈されることもあって現在の原子吸光分析では正確な分析が難しい。この分野に関係する人たちはコスト高になってもよいから感度が最も必要なものだと感じている〔I 102〕。一方，環境分析や公衆衛生分析では，しばしば，一日当たり数十～数百検体という多量の検査をする必要がある場合がある。このような場合，ある程度精度を犠牲にしても，迅速性が最も必要となる。

イメージアナリシス (Image analysis)

また，無機合成化学の分野においては，元素の分布を知る（イメージアナリシス）ことが重要なことが多い。この分野では主成分分析が多く，感度はそれほど高くなくてもよい場合が多い。もっとも，最近になって急速に発展してきた集積回路を含む半導体製造分野においては極微量のドープ成分の分布を測定する必要性が出てきており，イメージアナリシスの高感度化も必要となってきている。

平均濃度 (Bulk concentration)

日常分析において，また一方では，ある程度多量の試料中の平均的濃度を知ることが重要な場合もある。例えば，鉱石を評価する時には少ない試料量の分析では，目的元素の濃度にかなりの三次元的分布がある場合に誤った情報を与える危険性がある。試料調製法として伝統的に使われている四分法は，このことを避けるための方法の典型的なものである。

現場分析 (In—situ analysis)

また，一方，警察などの公的機関の検査における様に，現行犯を立証するために現場において可能な分析が重要となる場合がある。例えば運転者のアルコール検査，税関の麻薬検査，行政局による重金属や廃オイルの不法投棄物のチェック等。また，海洋調査や内陸地質調査などでは，試料を研究室に持ち帰るのに時間を要し，かつ次の移動先をその地点での分析値により判断する必要がある場合もある。このような場合は迅速で選択性の良い現場分析（in-situ analysis）が必要となってくる。

In-vivo分析，安定性 (In-vivo analysis, Stability)

また，人体の臨床検査では，人体に危害を与えないという点（in-vivo）が最重要因子である。他方，鉄鋼の欠陥の連続的な検査のような工程分析においては高温，振動，電気ノイズなどのような厳しい環境に対しても長期にわたって安定で信頼性が高いという点が特別な因子として加わる。

挙げれば限りがないが，このように応用分野の違いによって分析法または装置における重要度の高い因子は異っている。

高性能，コスト，機能性など (High performance, cost, function etc.)

また，次のような別な見方もできる。学術的な目的のためには，コストをほとんど無視してでも，ある特別な性能を有する分析装置を開発する必要がある場合がある。例えば，宇宙船搭載用の高性能，高信頼，小型の分光分析装置，考古学における同位体による年代決定用の質量分析装置，核融合プラズマの研究におけるプラズマの計測用高分解能分光器などは，一品ごとの特別設計の場合が多く，高価なものである。このような場合は，第一にその学術的目的に対し必要な性能条件を満足することが最優先の因子である。一方，多数の試料を大まかにチェックするような日常分析のための分析装置においては，上記ほどの高性能を必要としない場合が多い。例えば民間工場における排水中の重金属チェックのような場合。このような場合においては，むしろ分析装置の扱いやすさ，消費する電力，ガス，試薬が少ないこと，分析時の廃液，廃ガスなどの毒性が低いことなどが重要となる。また，装置のデザインの良さ，コスト当りの性能が高いことなども重要な因子となる。

5. 分析化学的方法の種類（無機の機器分析を主体として）(Kinds of instrumental analyses)

上に分析化学に関して種々の因子を考えてきたが，ここで現在の分析化学的方法を（本論文が無機分析に関するものであるので無機分析法を主体にして）これらの因子と結びつけて特徴づけてみよう。表１－５に分析法の大まかな分類を示す。

分光法の真髄 (Spectroscopic essence)

分光法の真髄は「分析対象物から生ずる電磁波や荷電粒子のエネルギー分散，または外部からそれらを与えて分析対象物との相互作用で生ずるエネルギー分散 ――スペクトルを通して，分析対象物に触れずにその組成や状態についての情報をいかに選択的に得るか」ということにあると思う。この志向は分光学の創始者達が分光鏡（Spectroscope）を覗いて遠く隔った太陽や星の中の元素を知った古から延々と今日まで生き続けており，種々の分光法の中に存在していると思われる。

種々の分光法のうち元素の分析法として用いられているものは，原子分光法，X線分光法，質量分析法，放射化学分析，分光光度法などである。

原子分光法 (Atomic spectroscopy)

原子分光法の最大の特徴は非常に高い選択性にあるといえる。気体状の原子における鋭い共鳴条件のためにこの過程での選択性は本質的に高く，実際の選択性は実質的には分散系の分解能で決ってしまう。通常の分光器で分解能は約50,000であるが，共鳴分光器を用いると500,000にも達する。この特徴は，元素を確実に同定する目的には非常に適しているものといえる。通常，試料はガス状原子にするため破壊される。したがって，原子分光法はそれ自体では形態分析法となり得ない。しかし，原子化という過程により試料は原子蒸気という一つの均質な相にされるので，原子分光法は試料の形態に対し広い受入れ体制を有しているといえる。高感度（ppm～ppb, ng～pg）ということも手伝って，これら二つの特徴は原子分光法がいろいろな分野に渡り広く普及した理由の主なものかもしれない。実際，スパーク，アーク発光分光法は，岩石，鉄鋼などの固体試料や液体試料中

Table 1-5 Rough classification of instrumental analytical methods

Spectroscopy;	Atomic spectroscopy, Molecular spectroscopy (UV, IR and visible photometry, Fluorometry), Raman spectroscopy, Xray spectroscopy (XFS, Auger electron), γray spectroscopy, magnetic resonance spectroscopy (NMR, ESR), Nucleo-chemical methods, Mass spectrometry etc.
Thermal analysis;	DTA, DSC, Thermal titrimetry etc.
Electrochemical; analysis	Voltammetry, Ion selective electrode, Polarography, Coulometry etc.
Chromatography;	GC, TLC, Ion chromatography, LC etc.
(Bio)chemical; analysis	Chemical sensor (gas sensor), Biochemical sensor (Enzyme sensor), Organic elemental analysis, Automated traditional chemical analysis (titrimetry) etc.

Features;
- Physical
- Physicochemical
  - Remote
  - In touch
- (Bio) chemical
  - Non-separative
  - Separative

- Non-destructive / Destructive
- In-vitro / In-vivo
- Continous / Batchwise

- Bulk / Distribution
- Absolute analysis / Calibration

の微量元素の迅速な定性分析法として広く使われてきている。また原子吸光分光法は工業分析，環境分析に広く適用されている。

しかし，原子分光法が種々の試料形態に対応できるとはいえ，試料中の複雑かつ多量のマトリックス成分から生ずる化学種によるバックグラウンド信号や干渉の問題がやっかいな問題として残っている。このことについては本論文の主テーマであるので後で再び詳しく述べる。

X線分光法 (Xray spectroscopy)

X線分光法のうち元素の微量分析法として広く用いられているのはけい光X線分光法であろう。この方法の最大の特徴は多元素同時分析が非破壊でできることにあると思われる。この特徴は，考古

学上の貴重な試料や宝石などの分析には最も都合がよい。また，岩石や無機合成物で試料の前処理が困難だったり時間がかかる場合にも都合がよい。しかし，深刻な問題として軽元素に感度が悪いことや，コンプトン散乱によるバックグラウンド信号が大きいなどのことがある。最近，陽子（粒子）誘起X線発光分光法（PIXE）〔I 12〕が，軽元素に対し本質的に励起断面積が大きく感度が高い方法として注目されてきた。しかし，この方法でも，生体試料のような複雑かつ多量のマトリックス中の微量元素の直接分析の場合には，バックグラウンド信号の問題はかなり深刻であり，またマトリックスの違いにより変化するため，試料マトリックスの調整に注意を払う必要があると思われる。

X線分光法のもう一つの重要な特徴は元素の分布の測定，即ちイメージ分析が可能なことである。電子やイオンのマイクロビームを分析対象物に当て発生するX線を測定する。このときマイクロビームを掃引することにより二次元分布を知ることができる〔I 13〕。これら，エレクトロンプローブマイクロアナリシス（EPMA）やイオン誘起X線マイクロアナリシス（IIXMA）は感度が比較的低いため微量分析には適さないが，無機合成物，合金，フィルム，岩石，集積回路などの表面および皮下のイメージ分析に広く用いられている。X線吸収を用いたイメージ分析の例としては最近，臨床医学の分野で画期的なものとして使われ始めた計算機断層写真法（CT-scanning method）がある。これにより人体の三次元的な検査が可能となった。例えば脳出血の治療の前に出血位置を正確に判断できるため的確な手術ができ，脳出血による死亡率の低下に大きく寄与している。

質量分析法 (Mass spectrometry)

質量分析法のうち元素の微量分析に用いられているのはスパーク源質量分析法であろう。特徴としてはイオンの質量を正確に決められることから（1ミリマス単位以下）選択性が高い，四重極質量分析計やイメージ検出器を用いると多元素同時分析が可能，イオンは原子，分子を問わないのでキャラクタリゼーションが可能などの数々のことが挙げられる。しかし，主にスパーク源の安定の悪さのため同位体希釈法などの方法を用いないと定量分析においてはあまり精度はよくない。いかに安定なイオン源を作るかが重要であると思われる。最近になって原子発光分光分析用に開発された高周波誘導プラズマ励起源を質量分析計の安定なイオン源として用いた報告もされている。〔I 103〕

X線分光法と同様，質量分析法にもイメージ分析の方法が最近開発されてきた〔I 14, I 15〕。イオンマイクロビームやレーザービームを試料表面に当て，生じた二次イオンを質量分析計で測定する方法で，ビームを掃引することにより像が得られる。イオンマイクロプローブ質量分析法（IMMA）または二次イオン質量分析法（SIMS）およびレーザーマイクロプローブ質量分析法（LAMMA）と呼ばれるこれらの方法は，電荷を直接捕集検出するため，X線光子を電流に変換する効率が比較的悪いEPMAやIIXMAなどの方法より感度が高く，より微量の分析にも用いることができるものとされている。

分光光度法 (Spectrophotometry)

分光光度法は公定法の中で種々の元素の分析法として用いられてきており，光吸収の媒体が溶液

状態で安定しているため信号測定時の精度が高くとれるという特徴を有している。また，無機，有機を問わず種々の化学種が測定できる。しかし，溶液状態では溶媒によるシュタルク効果のため試料の分子スペクトルは拡がりを生じ目的化学種についての選択性が悪い。したがって分光光度法ではいかに目的化学種に対して特異的なスペクトルを生じさせる試薬を作るかまたは見つけるかがキーポイントである。また高い吸光係数を与える錯体を生成すれば本法は高感度化される。この考え方で，もう一つの光度法であるけい光分光光度法において高吸光係数錯体を形成し，かつ光源に色素レーザーを用いることにより10^{-15} Mという超高感度を得た報告もある〔1〕。

放射化学分析(Radiochemical analysis)

放射線を使う分析法には次のような色々な方法があるが，いずれも核現象を利用している。放射線のエネルギー分散から同定を行えるが，そのエネルギーが高いため核現象を個数単位で追えることから感度が高い。また，非破壊分析が可能である。微量の放射性同位体から，自然放出される放射線を使う方法は，生体の代謝系路でのトレーサーや，^{14}Cによる考古学的試料の年代決定にみられる。原子炉または，さらに簡便なものとしてはAm−Beなどのような中性子源を用いる放射化分析は非放射性核を放射性にできるので種々の元素の微量分析に使われている。核共鳴を利用したメスバウァー分光法は，まわりの電子との相互作用に関する情報を与えるので状態分析に役立つ。

放射化学分析には以上のように色々な特徴があるが，放射線の人体への影響を考えると，日常分析法として使うには工夫が必要であろう。

電気化学分析(Electrochemical analysis)

電気化学分析は，分析化学種を含むイオンが電極表面上で化学反応に関与することによって生じる電流や電圧を測定するという点で，上に述べた種々の分光法に比べると化学的色合いが濃いと思われる。この方法の特徴は分析化学種を含むイオンの電荷を直接電気信号に変換できるので感度が高いことと，電量分析でみられるように，電気量とイオン量との間には直接的な関係がファラデー定数を介して存在するので重量分析のような絶対分析法が成立するということである。キーポイントはポーラログラフィーや種々のボルタンメトリーで見られるように，検出している電気信号が何のイオンに基くものかという選択性をいかに持たせるかであろう。最近のボルタンメトリー〔3〕やイオン選択電極〔5〕は高感度（ppm〜ppb）であり元素の痕跡分析に用いられる。また，有機，無機イオンの両方が測定できるので，カテコールアミンなどの生体物質の分析にも用いられる〔4〕。装置も電極と信号処理系を含むシンプルなものであり連続測定も可能である。しかし，分析対象物がイオンでなくてはならないのと，電極表面を常に新鮮にしておかなくてはならないという点で，固体や乳濁液のような試料や非イオン化合物を含む試料に対しては前処理を必要とする点が問題であろう。

その他の分析法(Other analytical methods)

上に述べてきた分光法，電気化学分析法は非分離分析に分類される。これらの方法では分離過程を含まないで，いかに直接的に目的とする情報を得るか，またその際に妨害となるマトリックス効

果を除去するかという点がキーポイントである。このことは，本論文の主課題もこれにかかわるもので，一つの重要な志向であると思われる。しかし，現段階においては，これらの方法のみでは選択性，マトリックス効果の除去は完全ではない。そこで，従来，手分析で用いられてきた酸分解，蒸留，沈殿など種々の化学的操作が不可欠となるが，これらの方法も現在の痕跡分析法に合わせて，汚染や損失を極力少なくするような改良がますます必要となるであろう。また酵素反応を含めた生物化学的方法ももっと取り入れられるべきであろう。一方，クロマトグラフ的な分離は例えばイオンクロマトグラフィーやキレートガスクロマトグラフィーのように無機元素を分離し，マトリックス効果を除去するのには有効である。また，熱分析を含めて他のいろいろな方法が併用され役立つ情報を与えることは言うまでもないであろう。

6. 原子分光法と原子分光分析 (Atomic spectroscopy and analytical atomic spectroscopy)

以上，分析化学に対する著者の見方を一般的に述べ，いろいろな方法について関係する因子を考えながら本論文が関係している原子分光法をとり巻く状況を見てきた。しかし，本論文の主題の位置付けを明確にするには，原子分光法自体について，著者の現時点での見方をもう少し詳しく論ずる必要がある。このことも前の一般論に相関付けながら行う。

現在，痕跡分析のための原子分光法は大まかには原子発光分光法，原子吸光分光法，原子けい光分光法に分類される。ところでこの分光法ということばであるが，種々の変形が使われる。英語でいうと，1)主に原理に関係することを示す場合は Spectroscopy（分光学（分光法）：もともとは分光鏡を示す Spectroscope から由来する），2)興味の中心が主に計測工学的問題にある場合には Spectrometry（分光法：もともとは Spectrometer を用いることから)または，検出器に写真乾板を用いる場合は Spectrography が，3)興味の中心が主に化学的処理過程を含む分析そのもの，または関係するソフトウェアーにある場合には Spectrophotometry（分光光度法），Spectrometric analysis（分光分析），Spectrohotometric analysis（分光光度分析），Spectrochemical analysis（分光化学分析）などが使われる。このように，ことば一つを取っても，三種類であることからもわかるように，分析化学的な原子分光法（日本ではこれを原子分光分析と呼ぶ）*も図１で示した三つの成分，即ち原理（理論），装置化（ハードウェア，工学，技術）および応用（ソフトウェア）からなっていることがわかる。表２にはそのうちの前者二つに関係するものを，分析化学的な原子分光法（原子分光分析）について示す。（応用分野については表１－４参照）

分析化学的な分光学者も，一般論で論じたように，これら三つの成分の調和（荷重のかけ方）に迷い悩むであろう。また，表１－２のところで論じたように一つの方法の開発過程の各段階を経る際も思い悩むであろう。では分析化学的な分光学者は過去において思い悩みながらどのような道をたどって現在に至ったのであろうか。

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* 以後，著者は両方を混用する。だが，分光法そのものに関したニュアンスが強い時は～分光法と書く。

Table 2 Components of analytical atomic spectroscopy

Spectroscopy	Atomization/excitation source
Atomic emission spectroscopy Flame photometry Arc/spark emission Inductively coupled plasma	Chemical flames (air-C_2H_2, air-H_2 etc.) Electric discharges Spark Arc DC, AC, RF, microwave Glow discharge Inductively coupled plasma Capacitively coupled plasma Microwave induced plasma etc.
Atomic absorption spectrometry	Electrothermal atomizer
Zeeman AAS	Cold vapor
Atomic fluorescence spectroscopy	Dispersion systems Detectors Electronics
Atomic magneto-optical rotation spectroscopy	Light sources (hollow cathode lamp, electrodeless discharge lamp etc.)
Multi-line method	

7. 分析化学的な原子分光法（原子分光分析）の歴史的背景(Historical aspect of analytical atomic spectroscopy)

Bunsen，Kirchhoff の炎光光度法 (Flame photometry by Bunsen and Kirchhoff)

良く知られているように，原子分光法を元素の同定法として提唱し研究を行ったのは19世紀後半における Bunsen と Kirchhoff である[I 16]。彼らは石炭ガス炎を原子化兼励起源として用い，その中に存在するアルカリ金属元素の色のついたD線を小さな分光鏡を通して観察した。彼らの論文は雑誌「Fresenius' Zeitschrift für Analytische Chemie」の第一巻[8]に載せられている。そこには彼らが用いたバーナー（Bunsen burner）と分光鏡がスケッチされており，また巻頭にはその装置で観察されたスペクトルのスケッチが着色されて載っている。これらは著者にとって誠に印象的で，機器分析の発祥を示す象徴のように感じられる。

Bunsen と Kirchhoff の方法即ち炎光光度法は今日でも，色ガラスフィルターを組み込んだ簡単な装置で比較的高い感度と精度が得られる方法として，臨床医学において臓器疾患の診断を目的とした体液中の Na や K の定量に日常的に利用されている。

Atomic emission spectroscopy

Atomic absorption spectroscopy

Atomic fluorescence spectroscopy

Fig. 2 Schematic diagrams of principle for three kinds of atomic spectroscopy (as for detailed theory, refer to the main text in Chapter 2)

さて，化学炎の温度はアルカリ金属元素やアルカリ土類金属元素のような励起エネルギーが低い元素の分析には十分であったが，その他の高い励起エネルギーの元素の励起には低過ぎた。図2に原子発光，吸光，けい光分光法の原理図を示す。図から分かるように原子発光では，励起準位のポピュレーションを多くすることが強い発光強度を与える，即ち感度を高くする。そのためには，励起源の高い温度が必要不可欠である。

スパーク，アーク発光分光分析 (Spark/arc emission spectroscopy)

1890年代から1930年代にかけてGerlach[9]を含む多くの分光学者はスパーク，アークなどの電気放電を高温励起源として開発，改良を重ねた。安定化や高感度化を目的としていろいろな型のアーク，スパーク用電源や電極構造が考案され原子発光分光分析は実用化されていった。その他にも，この方法を実用的なものにすることに貢献している重要な因子が二つある。一つは分光器の改良で，リトロー型を含むいろいろな型の高分解能分光器が考案されたこと。発光モードでは分光器の分解能は直接的に選択性に影響する。もう一つは，Nieps板から始まりdaguerreotypeを経て，写真乾板技術が発達したことである。写真乾板はいくつかのスペクトル線を同時に，また積分強度として記録できる。この考え方は，今や，光電子増倍管という応答直線性の良い検出器が用いられている中においても，ホトダイオードアレイなどのイメージセンサーという形で復活してきている。写真乾板という便利な検出器と，岩石，金属，水溶液などの種々の形態の試料を直接，原子化，励起できるという便利性はスパーク，アークによる原子発光分光法が今日まで元素の同定に広く使われている理由の一つであろう。

量子力学の登場 (Advent of quantum mechanics)

1930年代は量子力学が急速に発展した時期であった。量子力学は原子分光法に理論的ベースを与えた。また逆に原子分光法も量子力学に対し実験的確証を与える役目を果した。こうした理論的分野（図1の一成分）からのバックアップとニーズも上に述べた原子分光法の技術的，工学的な面（図1の別の一成分）の発展を促した。この状況は一般論で述べたように，分析化学に対して物理化学が理論的分野として大きく寄与した状況と類似している。一般論での分析化学の発展段階の分類に対応させて分類するとBunsenとKirchhoffの時代は分析化学的原子分光法の発達の第一段階であり，1930年代までのスパーク，アークによる原子発光分光法の確立期は第二段階と言えよう。

高温化学炎 (Chemical flames at high temperatures)

スパーク，アーク発光分光分析は元素の定性分析には便利なものであるが，放電の安定性が悪く定量分析には精度が十分とはいえなかった。第二次大戦後，いろいろな燃料と助燃ガスを組み合わせて，安定性にすぐれた化学炎の温度を上昇する試みが行われた[117]。高温の化学炎を発光分光法による定量分析のための励起源に使うという考えであった。こうして，亜酸化窒素－アセチレン炎，シアノゲン－アセチレン炎などが開発されたが，温度はせいぜい4000℃止まりであり，高い励起エネルギーを持つ元素の分析には広くは使えなかった。しかし，これらの種々の化学炎の研究はむだではなく次にやって来る原子吸光分光法の発展にとっては大いに役立ったのである。こ

れ以後，分析化学的原子分光法，即ち原子分光分析は，電子工学を含む技術的な面の急速な発展に助力を得て現在までの発展段階（第三段階と呼んでもよいだろう）に入る。表3に，この節で最初に分類した三種の分析化学的原子分光法（原子分光分析）（1）原子発光分光法，AES，2）原子吸光分光法，AAS，3）原子けい光分光法，AFS）の簡単な年表を掲げる。

Table 3 Brief chronology of analytical atomic spectroscopy

AES	AAS	AFS
1666 Light dispersion (Newton)		
	1802 Reversal line (Wollaston)	
	1815 Fraunhofer line (Fraunhofer)	
1860 Flame photometry (Bunsen & Kirchhoff)		
1890s-1930s Spark/arc-AES, various types of monochromator	1896 Zeeman effect (Zeeman)	1924 Atomic fluorescence (Nich
	1955 AAS concept (Walsh & Alkemade et al.)	
1961 Prototype of ICP (Reed)	1955-62 Basic development/many patents in Australia and New Zealand	
	1961 ETA (L'vov)	1963 Prediction of AFS (Alkemade)
1962-69 Basic development, detection limit (Fassel et al.)	1962-69 Explosive growth, commercially available systems	1964-69 Theory and basic development (Winefordner et al.)
1965-70 Optimization for low interelement effect	1969-76 Standardization	
1970- Mechanism study	1970- Commercially available EAT's, mechanism study	1970- A commercial available non-dispersive instrument, many instrumental improvements
	1971 ZAAS (Prugger, Hadeishi)	
1975-80 Explosive growth, commercially available ICP's, standardization	1976- Commercially available ZAAS, microprocessor	1975- Dye-laser AFS
1981 ICP-AFS	1982- New types of (separative) ETA?, trace characterization?	1981 ICP-AFS
1982- Small sample size, minituarization, detailed mechanism study, other types of plasmas?		1982- Removal of background scattering, ZAFS?, time-resolved AFS?

原子吸光分光法の登場 (Appearance of AAS)

1955年，Walsh[10]と Alkemade[I 18]らは別々に，原子蒸気を通過するとき共鳴光が吸収されるという現象，即ち原子吸光現象を分析法として使うことを提案した ── 原子吸光分光法。原子吸光現象は古くは1802年に Wollaston，1815年に Fraunhofer[I 19]によって太陽スペクトル中の黒線として発見され，Kirchhoff により理論的な研究がなされた。それ以来，この現象は分析化学には応用されなかった。だから Walsh と Alkemade らによる提案は古く発見された現象の150年振りの復活といえる。これは，ちょうど Bunsen と Kirchhoff の炎光光度法が，Newton による光分散の研究から180年以上も経てから出現したという状況に似ている。

原子吸光分光法の潜伏期

図2からもわかるように，原子吸光分光法では原子発光分光法のように原子の励起は必要でなく

試料から基底状態の原子を生成する，即ち原子化だけでよい。これは，低い温度の化学炎でも可能である。前にも述べたように，種々の化学炎は当時既に研究が進行していたので原子吸光分光法はすぐにでも普及するかと思われたが，実際にはなかなかそうは行かなかった。Koirtyohannが述べているように[16]1955～1962年の間はWalshの研究の場であった（出身はイギリス）オーストラリアと隣国のニュージランド以外の国の学会では原子吸光分光法は容易には受け入れられなかったようである。Walshは原子吸光分光法の特徴を理解してもらうため積極的にアメリカ合衆国を旅行したが障壁は高かったようである。Koirtyohannは1955～1962年の時期を原子吸光分光法の「オーストラリアとニュージーランドにおける潜行的育成（the development down under Australia and New Zealand）」と呼んでいる[16]。このように新しい方法が受け入れられるようになるまでには一定の期間が必要なようである。

原子吸光分光法が広く実用的な方法として受け入れられるには克服しなければならない技術的な問題があった。図2からわかるように原子吸光分光法の場合，光源光強度の変動は直接に信号のベースラインのノイズとなって現われS／N比の低下につながる。また，感度を得るためには光源光の幅が吸収線の幅より狭い必要がある。線幅が狭く安定な光源としての中空陰極ランプが実用化するまでには割合に時間を要した。それまでは，原子吸光分光計はなかなか普及するには到らなかった。このように，原理的にはすぐれていても，技術的な問題が支配的な障害となっていて一つの方法が実用的に確立されるに到らない場合も多い。（図1参照）

原子吸光分光法の急成長期 (Explosive growth period of AAS)

Koirtyohannによると[16]1962～69年は原子吸光分光法の急速な成長期であった。彼はこの時期を「原子吸光分光法のファン タイム」と評している[16]。この時期には，バーナー，噴霧器などの部分の改良が数多くなされた。また，湿式灰化，溶媒抽出などの化学処理も原子吸光分光法に適合するようなものが研究された。この時期に原子吸光分光法の原理と装置化およびソフトウェアーの基本的なところはほぼ研究され，それ以後の応用面での研究の基礎となった。（原子吸光分析の確立）

1960年代の終り頃から公害などの環境問題が益々深刻になる中で，重金属の日常分析の必要性が高まった。それにつれ原子吸光分析はスパーク，アーク発光分光分析に比べて定量精度が良い，装置が小型で安価，扱いやすいなどのことから急速に普及した。原子吸光分光分析では多元素同時分析は困難であるが，このことは普及の妨げにはならなかったようである。これは，おそらく環境分析においては，問題となる元素が事例ごとに限定されているため（例えば，水俣病では海水や魚貝類中の水銀というように），多元素同時よりも一元素分析（ターゲット分析 ── 表1－3参照）の方が多いためであろう。

原子吸光分光法の安定期 (Standardization period of AAS)

1970年代になると原子吸光分光分析はそれまでの分光光度法に加え元素分析に関する公定法の中に加えられた。これ以後，原子吸光分光法は分析法として安定期に入ったと考えてもよいだろう（原

子分光分析の標準化）。しかし，炎を使う原子化器は必ず溶液かそれに近い試料形態を必要とし，原子発光分光分析用アーク，スパーク励起源のように固体試料を扱えないという不満があった。

電気加熱原子化器の出現 (Appearance of ETA)

そのような不満を解消すると思われる原子化器が既に原子吸光分光分析の急速な発展期の前に提案されていた。1961年に L'vov は炎を使わないで，電熱により試料を原子にする原子化器を提案した[11]。炎を使う原子化器のように試料を霧にして連続的に導入するのではなく一定の少量試料を黒鉛などの管に入れ，管に電気を通じることにより試料を3000℃位まで加熱して原子化する。電気加熱原子化器の真髄は少量の原子蒸気を効率よく光路中の高温部分へ閉じ込めることにある。このことにより μℓ または mg という少量の試料で炎による原子化器より一桁位高い感度が得られる。また，試料を霧にする必要がないので固体試料をも原子化することができる。

電気加熱原子化器の発展と問題点 (Development in ETA and its problems)

このような特徴を持つ電気加熱原子化器は原子吸光分光分析による少量試料中の痕跡分析に最適だと考えられて，1970年代の初めから普及し始めた。こうして1970年代半ば過ぎ位までは電気加熱原子化器に関する数々の研究と報告がなされた。この時期は電気加熱原子化器にとってちょうど原子吸光分光法のファンタイムのような時期であったと思われる。

ところが，種々の実際試料への応用が進むにつれて，数々の問題が出され，メーカーの宣伝にうたってある程には，電気加熱原子化器による直接分析は容易でないことがわかってきた。その主な理由は本論文の主題である試料マトリックスによるバックグラウンド吸光と化学干渉である。この二つは炎を用いた原子化器にもみられるが，電気加熱原子化器ではさらに複雑である。このことに関しては後でまたいくらか詳しく述べるが，現在までのところ，この二つの問題に対する決定打はみられないように思われる。この二つの問題を克服することは電気加熱原子化器の普及にとって重要である。

原子発光分光法の見直し (Re-evaluation of AES)

さて再び原子吸光分光法のファンタイムである1960年の初めに戻ってみよう。この頃，即ち原子吸光分光法の花盛りの中で既に，幾人かの原子分光学者は原子発光分光法を見直しており，原子吸光分光法にはない数々の特長があることに気付いていた。図2の原理図から分かるように原子発光分光法では光源光を必要としない，したがって，原子吸光分光法のように信号のベースラインのノイズに光源光強度の変動が含まれず，検出器と電子回路だけのノイズになる。また，多元素同時の検出が容易であるなどの特長がある。

原理的に，原子発光分光法では励起状態の原子を多く作ることがいろいろな元素に渡って実用的な感度を得るためには必要であることは，1950年代における発光分光法用の励起源のための高温化学炎の研究のところでも述べた。したがって，この時期，いかにして化学炎のように安定でかつスパーク，アークのように高温の励起源を開発するかが，原子発光分光法を原子吸光分光法のように定量分析に使えるようにするための鍵であった。

ICPの登場と潜伏期 (Appearance and latent period of ICP)

1961年，Reed は，高周波誘導により大気圧で，放電が可能なプラズマを報告した[16]。これは，現在の高周波誘導プラズマ（ICP）の原型と言ってよいだろう。

Barnes によると[I 10]，ICP の初期の研究においてはとにかく，これを実用的なものにするために放電の安定化と検出限界の向上に力が入れられていた。この時期は原子吸光分光法の花盛りの時期で（1962－1969年）実際分析における試料マトリックスによる干渉の問題が浮かび上ってきている頃でもあった。そこで，当時の ICP が比較的，干渉を受け易かったことと，そのメカニズムの研究がほとんどなかったこともあって，定量分析法としてその後も（1975年頃まで）なかなか受け入れられない時期があった。これは，ちょうど原子吸光分光法が初めの頃，なかなか受け入れられなかったのと似ている。Fassel は1979年のハワイにおける Fisher 賞受賞の挨拶の中で[I 7] ICPのこの苦しい時期を次のように表現している。「Boumans は[I 8]『発光分光法による多元素同時分析 ── 玉座に上がるか，はたまた転落するか？』という命題を使った。私は Walsh 卿が使った『原子吸光分光法 ── 隆盛か沈滞か？』[I 9]という命題から『発光分光法－隆盛か沈滞か？』という命題を使いたい。」

共存元素効果の低減 (Reduction of inter-element effect)

1965－1970年に渡り，Fassel，Greenfield，Robin と彼らの共同研究者らは ICP の共存元素による干渉を少なくするため，その動作条件を詳しく研究した。放電，冷却，試料導入のための三つのアルゴン流の流量，放電用石英管の形状，高周波の電力および周波数などを選ぶことにより，高いエネルギーを持つドーナツ状の放電の中心を通して試料の霧が通過するようにした[18]。これにより，共存元素による干渉を著しく低くすることができた。1970年頃からICPの励起メカニズムの研究が始まっていたが，干渉低減については，当時（現在においてすら）完全には説明がされてなかった。恐らくこのことも一部関係して1975年頃まで依然として ICP は定量分析法として普及するには至らなかった。

ICP発光分析の急速な発展 (Explosive growth of ICP)

メカニズムがはっきりしないにしても ICP の上に述べた特長の実験的な報告は積み重ねられていった。原子吸光分光法が既に分析法として安定期に入っていた1975年頃から ICP は原子発光分光分析用の励起源として急速に市販品にとり入れられていった（ICP発光分光分析の確立）。この1975－1980年の時期は ICP にとって原子吸光分光法の1962－1969年におけるファンタイムに当たると言ってもよいだろう。Barnes によると[I 10]この時期には，ICP に関係した学術雑誌[22]やメーカーが急速にその数を増したということである。また，1980年にはアメリカ環境保護庁（EPA）により ICP 発光分光分析は水質分析法として認定された[I 10]。

こうして1980年代に入り，ICP による原子発光分光法はかつて原子吸光分光法が1970年代にそうしたように分析法として安定期に入りつつある。

歴史は原子発光分光法（Bunsen，Kirchhoff による炎光光度法，スパークアーク励起源）→原子

吸光分光法→原子発光分光法（ICP励起源）という繰り返しを経てきた。現在においては，これらの方法は共存している。

原子けい光分光法の登場 (Appearance of AFS)

さて，三度，原子吸光分光法の急激な発展期に戻ってみよう。この頃，原子発光分光法や原子吸光分光法とは異った原理が分析法にとり入れられていた。1962年の Alkemade の予言[I 21]の後，1964年に Winefordner と Vickers[15]は原子けい光分光法という新しい分析法を提唱した。原子けい光現象自体はそれより前，1924年に Nichols らにより報告されていた[I 22]。したがって，原子発光分光法，原子吸光分光法と同様に，原子けい光分光法の場合も古く発見され，利用されないでいた現象が分析化学的方法として復活したと言える。

1960年代の終りまでには，既に，原子けい光分光法について理論的な検討と，原子吸光分光分析用としてかなり研究が進んでいた化学炎を原子化器とした基本的な実験がなされた。図2から分かるように，原子けい光分光法には原理的に次のような特長があることがわかる。1）原子吸光分光法と同じく，原子発光分光法では必要な原子の熱励起を必要としない。2）光源を必要とするが原子吸光分光法でみられるような光源光強度の変動による信号のベースラインノイズはない。3）連続光源を使えば多元素同時分析が可能。4）光源光が線スペクトルの場合には分光器の分解能は低くてもよい。非分散でも可能。これらは初期の研究で実験的に確認された。

1970年代に入り，原子けい光分光法を分析法として実用的なものにするため種々の研究が行われた。スペクトル線強度の強い無電極放電管の開発や，原子吸光分光分析の原子化器として研究されていた電気加熱原子化器や還元気化原子化器との組み合わせなど。しかし，1980年までのところ，1970年に現れたフィルターを用いた6元素分析装置を除いては市販品は発売されなかった。

原子けい光分光分析の問題点 (Problems in AFS)

このように，原子けい光分光法は原子発光，吸光分光法に比べ実用化が遅れているのであるが，どうしてであろうか。Van Loon も言及しているが[I 23]，その主な原因の一つは，4πステラジアンに再輻射された原子けい光を効率よく回収するためには楕円球面のような特殊な光学系を必要とし，一般的な光学系では検出光のエネルギーが通常の検出器にとっては小さ過ぎる。そのため，無電極放電管や光電子計数器のような特別な装置が必要である。無電極放電管をすべての元素について作るのは封入する塩に適当なものがない場合もあるため困難である。また，封入物の熱による管内移動や石英への浸透のため安定性，寿命の点で実用品としては問題がある。

1970年代後半には，色素レーザーという波長可変でかつ強力な光源が実用的になってきた。これは確かに原子けい光分光法の光源として将来有望であるが，現在のところ，色素のメンテナンスと価格の面で実用的とは言い難い。

原子けい光分光法が実用的なものになる（原子けい光分析の確立の）ためにはもう一つ解決すべき問題がある。それは原子化の際，試料マトリックスから生ずる煙などの気体コロイドによる光源光の Mie 散乱や分子によるけい光などによるバックグラウンド信号である。これは，感度を上げは

うとして光源光を強くすればするほど大きくなる。

8. 応用分野での原子分光分析に対するニーズの変化 (Change in needs for analytical atomic spectroscopy)

以上に，分析化学的な原子分光法（原子分光分析）の歴史を述べてきたが，図1で言うと三要素のうちの原理的な面，表2で言うと分光法そのものについて主に関係付けてきた。分析法として原子分光法を位置付けるには，残りの二つの要素，即ち工学（技術，表2で言うと右半分の装置に関係する要素）と応用分野について言及する必要がある。本論文の主題であるところの，試料マトリックスによる「バックグラウンド信号」と「干渉」の問題は，試料形態に直接関係する。試料形態は応用分野で分析の必要性が生じている対象物の違いによって変化するので，まず応用分野でのニーズの質的な変化を考える必要がある。その後で現在の分析化学的な原子分光法が工学，技術的な面でそれにどう対応できているか，また問題点はどこにあるかを探る。

工業分析 (Industrial analysis)

第二次大戦後，工業界が急速に発展する中で，鉱石，石油などの原材料，また鉄鋼，金属，ガソリンなどの加工品中の元素の分析（工程分析，工業分析）は製品の均一性，品質を保つ上で不可欠なものとなりその必要性は高まっていった。工業製品のマトリックスは比較的単純で一定であり，また，分析目的元素の濃度も高く，分析に利用できる試料量も多い場合が多かった。

環境分析 (Environmental analysis)

1960年代の終り頃から，河川や海への廃液の流出，工場や自動車からの廃ガス，粉じんの放出，農薬の使用などから環境汚染が社会的問題となってきた。汚染物の排出を規制するためには，汚染物の分析をする必要があり，有機物と共に無機物の分析法に対する需要は環境分析の分野で高くなっていった。

重金属などの元素による公害の例は非常に多くみられる。例えば排水や農薬中の水銀による汚染，ガソリン中のノッキング防止剤としてのアルキル鉛からの鉛，メッキ工場からのクロム廃液，など。環境分析において，工場排水などはそのマトリックスが工業分析における試料のと似ていて比較的単純であるが，それが河川や海に入りヘドロとなったり，生物にとり込まれたりすると試料マトリックスはしだいに複雑となる。例えば，無機水銀化合物はマグロの肝臓により有機水銀に変化する。日本人などはさしみを食べることにより有機水銀に汚染する。野菜や果実の残留農薬からの汚染もあった。さらに汚染した母親の母乳から乳児が汚染する。1970年代においてこうした食物連鎖や代謝を通しての二次，三次の汚染経路の全体像を追究する必要性が高まり，益々分析対象試料のマトリックスは複雑になってきている。

生医学分析 (Biomedical analysis)

今日においては，がんや遺伝病の克服の研究にみられるように生命化学への関心が高まりつつあり，代謝を含む生命現象の解明が必要となってきている。生体中では有機物も，もちろん支配的な役割を果たしているが，種々の無機元素も重要な役割を果たしている[124]。生物がかつて海水と

いう主成分のアルカリ，アルカリ土類元素と種々の微量元素を含む溶液の中で発生し，現在でもその体液組成は海水に類似していることを考えると上のことは当然のことかもしれない。

生体の中で微量元素はその摂取量により毒にも滋養にもなって種々の作用をする〔I 24，I 104〕。例えば鉄，ヨウ素，銅，亜鉛，マンガン，コバルト，モリブデン，セレン，クロム，スズなどは，ppb～ppm 程度の微量必須元素で不足すると脱毛などの欠乏症が生ずることが知られている〔I 24〕。水銀，カドミウム，鉛，ヒ素などは現在までのところ不必要で毒性元素とされている。セレンなどは水銀毒に対する下毒剤とみなされている〔I 24〕。しかし多過ぎた場合には牛の旋回症を引き起こす〔I 24〕。水銀，金，銀，ニッケル，ケイ素，マグネシウムなどは発がん性を有することが認められている一方，白金や銅の錯体はアスコルビン酸などの存在下で制ガン作用があることも知られている〔I 24〕。中国のニュースは中国のある特定の地域で異常に高い食道がんの発生率が，その地域でのモリブデンが極端に少ない土壌で育成された野菜を食べていることに関係があることを報じていた。Margoshes と Vallee（医学博士で，原子発光分光分析の研究もした）はこのような微量元素の生体中での複雑な作用を解明する上で重要な物質として，メタロチオネインというシスチンを含むタンパク質（分子量＝6000～10000）と金属との錯体の存在を指摘した〔I 25〕。このように微量元素の生体高分子との錯体は生体中で代謝，酵素反応，ホルモン作用などの過程で，微量で効き目のあるスパイスのような役目をしているのかもしれない。余談になるかもしれないが，そうだとすると，その結果生ずる臨床医学上の症状にも微量元素の濃度が関連している可能性がある。したがって，多元素の濃度パターンと症例との間の相関をとることができれば，体液分析により，今までより正確な診断ができるかもしれない。従来は，器官異常の検査のために，体液中の主成分であるナトリウム，カリウムの濃度が炎光光度法により分析されているのが圧倒的に多い。

直接分析と試料マトリックスの複雑化 (Direct analysis and complication in sample matrix)

さて，このように生命現象の中で微量元素は重要な役割を果たしていることから，生命現象の研究において，微量元素の分析は益々，重要なものになってくるものと思われる。ところで，生体試料の分析においては，得られる試料が微量である場合がしばしばある。例えば細胞レベルであったり，元の試料量が多くても，それから抽出した量が μℓ や nℓ オーダーであったりする。また，微量元素の濃度も生体試料においては ppb レベルかそれ以下であることが多いため試料の前処理過程において分析目的元素の損失や汚染の危険性は高い。したがって，前処理なしの直接分析が必要となってくる。

工業分析，環境分析，生医学分析となるにつれ試料マトリックスがしだいに複雑となり，分析目的元素の濃度も低くなってくるが，このような試料の直接分析においては，試料マトリックスの妨害が著しくなってくる（表4を参照）。原子分光分析における妨害のうち最も深刻で克服すべきものは本論文の主題であるところの「バックグラウンド信号」と「共存元素効果を含めた干渉」だと思われる。（表4を参照）

では，この二つの問題に関して，分析化学的原子分光法（原子分光分析）は現在までのところど

のような状況にあるのだろうか。以下に探ってみよう。

Table 4 Needs for the direct analysis, relevant problems and main subject

9. 分析化学的原子分光法（原子分光分析）の「バックグラウンド信号」と「干渉」の問題に関する現在までの状況 (Current status of analytical atomic spectroscopy for background signals and interferences)

化学炎原子化器 (Chemical flame atomizer)

空気－アセチレン炎，亜酸化窒素－アセチレン，空気－水素炎などの化学炎による原子化器は広く原子吸光，けい光分光分析で用いられてきている。通常，分析試料を前処理をして溶液かそれに近い状態にしてから，噴霧器で霧状にして炎に導入するが，迅速性，簡便性を重視する場合や，前処理によって濃度が下がると感度の点で困る時には試料の懸濁液や乳濁液を直接噴霧する場合がある。また，懸濁液や乳濁液を調製しにくい場合や調製できても噴霧が困難な場合には，試料をカプセルに入れたり，火薬と混ぜたり[I 26]，Delves Cup 法[I 27]のように白金皿にとったりして，炎の中へ直接導入する方法がとられる。また，前処理による希釈をカバーするためやマトリックスを単純にするために目的元素のキレートを抽出する場合には有機溶媒が化学炎に噴霧導入される場合が多い。このような場合，多量の試料マトリックスが炎中で完全に分解せず，炭素の微粒子やNaClなどの非原子種が多く存在する。これらは，連続スペクトル的に光源光を散乱したり吸収したりする。これらは原子吸光分光法においてはバックグラウンド吸光を，原子けい光分光法におい

てはバックグラウンド散乱光を与え，信号に正の誤差を与える。

一方，試料マトリックスによる干渉について言えば，化学炎による原子化器では以下のようなものがある。NaClのような無機塩や硫酸，または糖類などが試料溶液中に高濃度で含まれていると，粘度が高くなり噴霧器での噴霧効率が下がる。また，霧の粒径が大きくなって炎の中での脱溶媒速度が遅くなり原子化率が下がるため信号強度に負の干渉を与える。一方，アルミニウム[128]やリン酸[101]イオンが共存する場合，アルカリ土類元素の空気－アセチレン炎による原子吸光分光法においては負の干渉がみられる。これらは化学炎中での化学反応により複雑な耐火性化合物を作ることによるものと考えられている。このような干渉は化学干渉と呼ばれているが，クロムと鉄の間の相互干渉のように炎の条件，クロムの原子価の違いで複雑に変化するのも知られている[105]。本論文の第2章でもクロムと鉄の間の化学干渉については詳しく取り上げている。

化学干渉，特に耐火物生成が原因だと考えられるような干渉を軽減するためには化学炎の温度を上げて原子化を促進させてやればよい。このような目的で，亜酸化窒素－アセチレン炎（温度は最高で約3080℃）がよく用いられる。ところが，一方，高い温度ではアルカリ土類元素のように容易にイオン化する元素は，共存するアルカリ元素や目的元素以外のアルカリ土類元素から，信号が増加するという正の干渉を受けることが知られている[100]。これは，炎の中で共存元素の電離により自由電子数が増加し，電離が抑制される結果（ルシャトリエの法則），目的元素の原子の数が増加するためだと考えられている。

電気加熱原子化器 (Electrothermal atomizer—ETA)

前節の歴史のところでも述べたように，電気加熱原子化器は溶液以外の種々の形態の試料を原子化できるし，試料量が微量でよいという特長を持ちながらも，試料マトリックスによるバックグラウンド信号が実際の分析における一つの大きな問題である。酸素を含む活性ラジカルが多く存在する化学炎と違って，電気加熱原子化器は，高温発熱体である黒鉛や金属（タングステンやモリブデンなど）を酸化から保護するためアルゴンなどの不活性ガス中に置かれている。そのため，生体試料などを直接原子化しようとする際には，煙が多量に発生し，光源光はMie散乱されてしまい，原子吸光分光法ではバックグラウンド吸光が，原子けい光分光法ではバックグラウンド散乱がみかけの信号として生ずる。有機マトリックスなどのバックグラウンド信号を生ずる成分を取り除くために，通常は原子化の前に低い温度で試料の炭化や灰化を加熱原子化器中で行う。しかし，元素自身やその塩の蒸気圧が高い元素はこの過程における損失が多くなり正しい分析結果は得られなくなる。例えば血液の直接分析の場合，炭化の過程で還元力の強い炭素が残渣として残るため，試料中の水銀やカドミウム化合物などは400～500℃以上の温度では蒸気圧の高い0価の金属に還元されほとんど揮散してしまう場合がある。

加熱原子化器においては，化学炎のように噴霧器における効率の変化による干渉は本質的に存在しない。また，雰囲気ガスであるアルゴンは原子化の過程での反応に関与しないので，種々の活性ラジカルのある化学炎の中での原子化より加熱原子化器での原子化の方が単純であると考え得るか

もしれない。ところが実際には，加熱原子化器での原子化機構は場合によってはそれほど単純ではなく，また，共存物質による化学干渉もかなり複雑であることが多くの実際分析において，分ってきた。このことは本質的には主に次の事に起因しているものと思われる。即ち，発熱体の温度は，電力を投入してから瞬間に一定の温度にはならず，ある時間をかけて上昇し平衡温度に到達する。この過渡的な段階で試料の蒸発，分留，発熱体との相互作用，発熱体への浸透，共存物質との反応などが複雑に組み合わさって起る。さらに，生成した原子蒸気の光路中での分布は原子の相互拡散係数，気相での共存化学種との反応，発熱体の温度分布，キャリヤーガスの流路，流速などにより，時間的にも空間的にも変化する。電気加熱原子化器におけるような回分的な原子化過程においては，これらの要因はかなり直接的に信号ピークの高さと形状に影響するものと思われる。

上記の要因に関係して，電気加熱原子化器を改良するために種々の試みがなされている。例えば，Gresser らは大容量のコンデンサー放電を用いて発熱体温度の立ち上がりを速くした〔I 30〕。L'vov は発熱体である黒鉛管内に試料を載せる板を置き，板が囲りの黒鉛管からの輻射熱で昇温するようにした〔I 31〕。このような傍熱型にすることにより試料接触部の温度分布を少なくした。温度の立ち上がりは遅くなるが，板が原子化温度に達するころ囲りの黒鉛管はそれより高い平衡温度に到達しているため試料から発生した化学種は気相状態で時間的に変化しない一定の温度という環境に置かれる。その他の改良方法として，発熱体である黒鉛管への試料の浸透による汚染を防ぐため管の内壁をパイログラファイト化したり〔I 105〕，炭化タンタル化したり〔I 106〕する試みや，試料の霧を連続的に電気加熱原子化器へ導入する試み〔I 32〕がなされている。しかし，複雑なマトリックスの試料に対し種々の場合に広く適用できる方法は少なく，依然としてバックグラウンド信号，複雑なマトリックス効果，信号強度の再現性を含め，電気加熱原子化器の実際分析での使いにくさは残されている。この問題を克服するための鍵は前述の不安定要因（温度の変動，分留など）をいかに制御するかにあると思われる。

このように加熱原子化器のむずかしい面に接した時には，連続導入型の「噴霧器－炎」による原子化器が，条件設定が比較的容易であり安定な信号が得られるという点で見直される場合もある。このようなことから，生体試料などのように複雑なマトリックスを含む微量の試料の分析のためには，加熱原子化器を改良するという方向とは別に，噴霧器－炎による原子化器を使う方法を改良しようとする方向もある。微量試料の前処理過程では特に，目的元素の汚染，損失が問題になるが，高圧ポンプなどでそれを極力防ぐ。そして，「一滴法」という方法で数十～数百 $\mu\ell$ の少量溶液を炎に導入する〔I 29〕。試料処理にはある程度時間を要しても原子化器での条件設定の時間が電気加熱原子化器の場合よりも少なくて済むから良い，という考え方であろう。

プラズマ励起源 (Plasma excitation source)

分析化学的分光法の歴史のところでは原子発光分光分析の励起源として ICP をもっぱら取り上げた。しかし，ICP が開発されるのと並んで，マイクロウェーブ誘起プラズマ（MIP）〔I 34〕，容量結合性マイクロウェーブプラズマ（CMP）〔I 35〕，グリムランプ〔I 36〕などのグロー放電プ

ラズマ，プラズマジェット[I 37]を含む直流アークなどの種々のプラズマ励起源が開発，研究された。これらのうちCMP，直流アークなど一部市販されているものもあるが，ICP程には広く普及していない。その主な理由は，ICPでは他のプラズマ励起源に比べて，試料マトリックスによる放電安定性の低下と共存元素による干渉が非常に少ないということであろう。ICPのこの特長の鍵は電力が大きい（数kW）ということとドーナツ状の高温プラズマ（約10000K)の中心部に試料の霧が導入されることにあると思われる。試料はドーナツの中心部を通過する際に，囲りの高温プラズマから十分なエネルギーを受ける。このことをもう少し詳しく，他のプラズマ励起源と比較しながら考えてみよう。

プラズマの温度 (Plasma temperatures)

プラズマを特徴付ける上で温度は重要なパラメータであるが，詳しくは本文の第2章でも述べるように四種類の温度が考えられる。化学種の並進運動のボルツマン分布で与えられるものが並進温度，振動運動のそれが振動温度，回転運動のそれが回転温度，化学種の軌道電子のエネルギー分布で与えられるものが励起温度である。前者三つの温度はガス温度と呼ばれる。アルゴンのような単原子ガスでは振動および回転温度は存在しない。

化学炎のような大気圧で低温の（放電プラズマに比べて）ガス体では四種類の温度はほぼ同じになる場合が多いが，放電プラズマでは励起温度がガス温度より高くなる場合が生ずる。この傾向は振動，回転の自由度を持たない希ガスのような単原子ガスのプラズマの方が窒素プラズマより著しい。また，減圧プラズマが常圧プラズマより著しい。さらに，この二つのことは，四種の温度が全体的に高い程，顕著になるようである。

上のことはプラズマ励起源の特性を複雑にする一因でもある。導入された試料を完全に分解し原子にする，即ち高い原子化率を得るためには高い並進，振動，回転温度，即ちガス温度および，それらの系のエネルギーの絶対量が大きいことが必要である。一方，強い原子発光を得るためには高い励起温度が必要となる。

MIP，CMP，ICP

このことをMIPとICPについて考えてみる。MIPはICPに匹敵する感度を，またヘリウムーMIPなどは励起エネルギーの高いハロゲン元素についてはICPより高い感度を与える[I 39]。実際にMIPは少電力でICPより高い励起温度を持つ場合が多くある。これだけを考えるとMIPは能率のよい高感度励起源であるが，有機物を含む多量の試料マトリックスが導入された時にはガス温度が急落するため原子化率が低くなり非原子種からのバックグラウンド発光が避けられないという欠点がある。時には放電自体が消えてしまう。これは本質的には投入エネルギーが低い（～200W）ためで，それの大きい（1kW以上）ICPは上記のMIPの欠点を回避している。

投入する絶対エネルギーが大きいということに加えてICPの,ドーナツプラズマの中心を試料が通るという特徴は，投入エネルギーを有効に試料に伝える点で有効と思われる。CMPでは電極中心上に高いエネルギーを持つプラズマコアが生成し，その反発力により試料がその中に入れないため十

分なエネルギーを受け取れない。そのため，有機溶媒などを多量に導入すると未解離の化学種からの強い発光がバックグラウンド信号を与える。

エネルギーの高いプラズマ領域へ試料を導入することは共存元素による化学干渉を少なくするためにも重要である。高いガス温度により化学干渉による原子化率の低下を防ぐことができる。ICPのドーナツプラズマはこの点についても有効である。

イオン化し易い元素による干渉が少ないということもICPの特徴である。CMPやMIPではこの種の干渉が著しい。この違いはやはりエネルギーの高いプラズマ領域の中へ試料が入るかどうかに起因しているようである。ICPの完全な機構は明らかではないが，エネルギーの高いプラズマ領域内では自由電子密度が高く，干渉元素の原子のイオン化による自由電子密度の変動はわずかなため，目的元素の原子のイオン化反応の平衡がわずかしか変化しないということが一因として挙げられている。このことは本論文の主題に深く関係があるので第二章においてさらに詳しく述べる。

ICPと試料マトリックス (ICP and sample matrix)

ICPは上述のような利点を持つが，生体試料のように試料量が少なく，試料形態および試料マトリックスが複雑な試料の分析ではいくつかの問題が生ずる。

ICPも化学炎による原子化器と同様に，試料導入には噴霧器を利用しているので，試料溶液の粘度の違いによる噴霧効率の変化に起因する干渉は避けられない。粘度が高過ぎると噴霧が不可能になる。最近，高粘度溶液やスラリーなどをも噴霧することができるBabington型噴霧器の利用なども報告されているが[I 10]，試料マトリックスの違いによる噴霧過程での干渉は避けられない。

先に述べた電気加熱原子化器をICPに取り付けることによって，溶液以外の形態でかつ微量の試料の導入を可能にしようとする試みも報告されている[I 40]。しかし，生成した蒸気がICPと電気加熱原子化器の連結部に析出するという問題があり満足な結果は得られていない。Salinら[I 41]は粉末試料を黒鉛管に詰めて，ICPのプラズマ中心へ入れるという方法を報告している。この方法は上記の析出の問題を回避している。(よく考えるとICP以前の発光分光分析用励起源であるスパーク，アーク励起源とよく似ていることに気が付く。このように，手法開発においては古い型の考え方が新しい形となって現われることがある。(表1－2のフィードバックを参照))しかしこのような方法では多量の試料マトリックスが導入されるため，原子化率が下がり，分子発光によるバックグラウンド信号と化学干渉が問題となると思われる。

生体試料のような複雑なマトリックスを含む試料のICPの分析では他に二つの深刻な問題がある。

一つは，共存元素として多量に含まれるカルシウムやマグネシウムからの発光線による迷光が，強いバックグラウンド信号となって現われることである[I 22]。このため，迷光が十分低い特別な分光器が必要となる。もう一つの問題はICPの動作条件によっては，励起，イオン化過程に起因するところの共存元素による干渉が最小になるプラズマの観測位置が分析元素ごとに異なるという点である[I 42]。これは共存元素の量が多くなればなるほど著しくなるものと思われ，生体試料のよう

な多量のマトリックスを含む試料の多元素同時分析での最適観測位置を決める際には支障となるであろう。BarnesのICPの総評の中にICPの応用分野の比率が載せられているが，水質分析に比べて生物学，医学方面での比率は少ない（10％以下）。このことは，上記の理由によるところが少なくないと思われる。

10. バックグラウンド信号と干渉を除く方法 (How to remove the background signals and interferences)

方法の分類 (Classification of methods)

前節で，現在の分析化学的原子分光法においては試料マトリックスに起因するバックグラウンド信号と干渉の問題が解決しなくてはならない重要な問題であることを論じた。この節ではこの二つの問題を解決または軽減すると思われる方法について将来的な方向をもいくらか含めて論ずる。この内容は，次節で述べる本論文の主題（原子磁気旋光分光法と多線法）の位置付けにとって，一段と直接的な背景を成すものである。

表5に著者なりに分類した方法を掲げた。分類は次の要素から大まかになされている。a）試料を前処理なしで直接原子化（＋励起）する方法か，前処理をする方法なのか。b）化学的方法，物理化学的方法，物理的（分光学的）方法のいずれによるのか。c）試料マトリックスと目的成分の分離を行う過程を含む方法なのか含まない方法なのか。d）バックグラウンド信号や干渉を除去する方

Table 5 Methods for correction/removal of background signals and interferences

Indirect	Chemical treatment/removal of B.G.S./Int.	Acid digestion, alkali fusion, solvent extraction, electrolysis, ion-exchange, co-precipitation, floatation etc. Matrix control (interference suppressor)/batch and flow
	Physico-chemical separation/removal of Int.	Ion chromatography, chelate and halide GC
Direct	Physico-chemical removal of B.G.S./Int. on excitation	ICP
	Physico-chemical separation on atomization/removal of B.G.S./Int.	Super high temperature GC separation atomizer (GC, diffusion, reaction column, fractional vaporization)
	Spectroscopic (physical) correction/removal of B.G.S.	D_2 lamp method for AAS (AFS) Zeeman AAS Sequential slew scanning (SSS) for AES/AFS Vibrating/rotating quartz disk Image sensors(SIT, visicon, photodiode array) AMORS (the atomic Faraday effect) Atomic Voigt effect Zeeman AFS?
	Spectroscopic correction of Int.	Multi-line method ––– elucidation of mechanisms

B.G.S. = background signals, Int. = Interference

法なのか補正する方法なのか。

試料の化学前処理による除去 (Removal by chemical pre-treatments of sample)

表5の最上段に掲げてある方法は前処理を化学的方法で行いバックグラウンド信号や干渉の原因となる試料マトリックスを除去またはその形態を変える方法である。酸や酸化剤などによる分解，アルカリ溶融などが処理方法として用いられてきた。また，共沈，電解，イオン交換，溶媒抽出，浮選などの方法が上記の方法と組み合わせて，または単独で使われる。

また，簡便な方法として試料に添加剤を加えて試料マトリックスを変えて（マトリックス調整）干渉を抑えるやり方もある。例えば原子吸光分光分析でみられるマグネシウムやカルシウムに対するアルミニウムやリン酸イオンの化学干渉は過剰のストロンチウムやランタンを加えることにより抑制できることが報告されている〔I 45〕。これは，測定目的元素が干渉剤と炎中で複雑な耐火性化合物を生成するのを，測定目的元素より容易に耐火性化合物を作る元素を加えて防ごうとすることに基いている。マスキング剤としてオルトフェナントロリンを過剰に加え，バリウムに対するアルミニウムやクロムに対する鉄の化学干渉を抑制した例も報告されている〔I 46〕。高温炎中でみられるイオン化率の変動による干渉を過剰の目的元素よりイオン化し易い元素を加えて抑制する方法も報告されている〔100〕。自由電子の増加により目的元素のイオン化が抑制されかつ干渉剤のイオン化による自由電子密度の変動が抑えられるため干渉が軽減されるものと思われる。この方法をCMPに適用した例もある〔I 47〕。また，この他電気加熱原子化器による鉛の分析の際，試料の塩形態の違いにより複雑に変化する原子吸光ピークをそろえるためにチオ尿素を添加する方法も報告されている〔I 48〕。

マトリックス調整の方法をさらに簡便で，かつ少量の試料に適用することができるようにするため，最近，調整剤の流れの中に $\mu\ell$ オーダーの試料溶液を注入する方法が研究されるようになった〔I 49〕。前に述べた一滴法〔I 29〕に比べると，目的元素の濃度が希釈されてしまうという欠点はあるものの，高い粘度の試料も導入でき，マトリックス調整により，化学干渉やイオン化干渉が自動的に抑制できるという利点がある。

このような流体の中で前処理しようとする方法に分離という項目を付け加えたものとしてクロマトグラフィーがあるが，原子分光分析と組み合わせる方法として典型的なものはイオンクロマトグラフィー（IC）〔50〕と金属キレートや金属のハロゲン化物や水素化物のガスクロマトグラフィーであろう。クロマトグラフ的分離を原子スペクトル法に組み合わせることは，原子分光法自体が無機元素の分子形態についての情報を与えないという欠点を補う点でも重要な意味を持つものと思われる。

以上の方法は試料を原子化器や励起源に入れる前に化学的方法で組成を単純化することにより測定上の妨害を除こうとするもので，伝統的な化学手分析の方法が活かされていて，化学的色彩が濃いといえる。これらの方法をかつての主成分分析から，近年の痕跡分析に適合するように改良して新しいものにする追究も一つの重要な方向であると思われる。

前処理なしの直接原子化，励起 (Direct atomization/excitation without pre-treatments)

しかし，現状においては化学的な前処理を行う過程では前にも述べたように汚染，損失などの問題が，特に微量試料中の低濃度元素の分析の際には完全には避けがたいものと思われる。そこで，前処理なしで試料を直接原子化（＋励起）し，生ずるバックグラウンド信号と干渉の問題はそれ以降の段階で除くかまたは補正しようというような，どちらかと言えば物理的な発想からの方法が浮かび上がってくる。これには大きく分けて二つの方法がある。一つは，バックグラウンド信号や干渉を生じさせないまたは軽減するような原子化器や励起源を開発することであり，もう一つは，生じたバックグラウンド信号や干渉を分光系や信号処理系で除去または補正するという方向である。（表２の分類参照）

励起源の改良による除去 (Removal by improvement of excitation source)

前者の例としては，前節で述べたICPが挙げられる。高いエネルギーで原子化率を高くし分子発光と化学干渉を除いている。また高い電子密度によりイオン化干渉を軽減している。密度の高いプラズマ中に試料をいかにして閉じ込めるかが鍵であるが，著者らが報告した熱中空陰極プラズマ[I 107]もそれを目指し，かつICPでは扱いにくい溶液以外の形態の微量試料を取り扱えることのできる励起源である。

原子化器の改良による除去 (Removal by impovement of atomizer)

原子化器の改良でバックグラウンド信号や干渉を除こうとする新しい試みとしては次のようなものがある。Van Loonは[I 152, I 153]中空陰極放電で観測された原子とバックグラウンド信号の時間的分離[I 154]が直接分析に有効に利用できることを強調している。試料を原子化器で原子化した後一度トラップすることにより試料マトリックスを単純化しようとする試みもある。例えば水銀の加熱気化－金アマルガム法もその一つであるし，空気－アセチレン炎中に水冷管を置き炎を通してできる生成物をその表面に析出させる方法[I 53]も報告されている。しかし，これらの方法ではトラップ効率が試料マトリックスの組成の違いにより大きく変化することが避けられない。

そこで，トラップ時に分離するのではなく原子化時または原子化直後に分離すればよいということになる。電気加熱原子化器では分留の問題を前に指摘したが，これを含めて，形態の異なる塩から発生する原子や分子の蒸気が分離することを利用して光学的測定時の系を単純にしようとする例もある。花村は電気加熱原子化器－CMP発光分光装置で Pb－PbO, Hg_2Cl_2－$HgCl_2$, As_2O_3－As_2O_5, Si－SiO（左の方が先に発光信号を与える）からのピークを分離した[I 108]。その他にもTlとCdのピークを電気加熱原子化器－非分散原子けい光法で分離した例[I 109]，電気加熱原子化器－MIP原子発光分光法でZn，Cu，Ni，Coなどの塩化物や硝酸塩について，種々のピーク分離を観測した例[I 110]などがある。

しかし，これらの方法は原子化器の過渡的温度上昇で起る分留や反応の違いを利用しているため複雑なマトリックスを含む試料に広く適用するためにはかなりの工夫が必要であると思われる。そこでガスクロマトグラフ的な分離をも含めたもっと積極的な分離方法が必要となる。

合金中の金属成分を気化し分離する試みはガスクロマトグラフィーの分野で報告されている。DeBoer は LiCl をコートした海砂をつめ，620 ℃に加熱したカラムを用いて Zn－Cd 合金中の Zn を除去し Cd の精製を行った〔I 111〕。Sokolov らは超高温ガスクロマトグラフィーと称して種種の合金中の成分の分離を，けいそう土，黒鉛粒，シリカゲルなどをつめ，700～1350℃に加熱したカラムを用いて分離した。感度の低いダイヤフラム検出器を用いており，目的は主に合金中の主成分分析に限定されていた〔I 112，I 113〕。

柳沢ら〔I 114，I 115，I 116〕および著者ら〔I 117，I 118〕は上記の方法を原子分光法に応用し元素の痕跡分析を可能にすると同時にバックグラウンド信号を与える成分を除去または分離する目的で分離原子化器を考案した。活性炭をつめた石英，ステンレス，アルミナ管を900～1250℃に加熱したカラムにT字状の吸光管を取り付けたものを原子化器とした。毛髪や木の葉などの生体試料中の水銀やカドミウムの原子吸光分析について検討した結果，かなり多量の（～100 mg）の試料を直接原子化してもバックグラウンド信号を与える煙などはカラムを通る間に水性ガスなどの透明ガスに変化するためバックグラウンド吸光は生じないということを報告している。また，EDTA をマトリックスとして含む試料の場合は NO によると思われるバックグラウンド吸光が見られたが，水銀のピークとは分離することを報告している。

著者らはガラス状炭素の長管原子化器を用いてアルゴンや窒素中のカドミウム及び亜鉛の拡散係数を測定したが〔I 119〕，1200～1500℃の温度において二つの金属の拡散係数間でかなりの差が生ずることを明らかにしている。また，拡散係数の違いをバックグラウンド信号を与える成分または干渉元素を含む蒸気と分析目的元素との分離に利用できることを提案した〔I 117〕。太田らは主に共存元素間の干渉を除くことを目的として，長モリブデン管原子化器を用いることにより銅，ナトリウム，マンガン，マグネシウムなどの原子蒸気の分離を行った〔I 120〕。分離ができる理由として，原子蒸気の拡散係数の違い，モリブデン管との反応などの種々の現象を挙げている。

分光学的方法による除去，補正 (Removal/correction by spectroscopic ways)

バックグラウンド信号と干渉の問題に対処する方法としては最後に分光学的方法がある（表5）。表2に掲げた分析化学的原子分光法を構成する成分で言うと，上述の方法が原子化器や励起源の改良に関係するものであるのに対し，分光学的方法は分光法の原理，即ち分光学そのものの応用とそれに関係する光学系，信号処理系の開発に深く関係している。分光学的方法としては次のようなものがある。

D_2 ランプによるバックグラウンド吸光補正 (Correction of background absorption with D_2 lamp)

原子吸光分光法においてはバックグラウンド吸光の補正法としては重水素放電管を用いた方法〔I 54〕が広く用いられている。分光器の光学的透過帯域幅は原子吸光線の幅より遥かに広いため，重水素放電管から出る連続光が原子によって吸収される割合はほとんど無視できる。ところが，ドップラー拡がりを起こした分子バンドによる吸光や煙などによるMie散乱は分光器の帯域幅以内では波長に関してほぼフラットな吸光特性を示すので，重水素放電管からの光は吸収される。一方，中

空陰極ランプからの光は線スペクトルであるため原子吸光，バックグラウンド吸光の両方を受ける。そこで，後者の吸光度から前者の吸光度を減ずれば正味の原子吸光による吸光度が得られる。しかし，この方法では，重水素放電管と中空陰極ランプからの光のエネルギーが元素によって大きく異なるためランプのゲイン調整を元素毎にしなくてはならないことと，二つのランプからの光束を一つの軸上に乗せなくてはならないというわずらわしさがある。特に後者の場合，完全に同一軸上に乗せるという光学調整は困難であり，わずかなずれが生ずるためにバックグラウンド吸光の補正に誤差を生ずる。この種の誤差は，バックグラウンド吸光を与える蒸気と原子蒸気の空間的分布が異なり，それが時間的に急速に変化するような電気加熱原子化器の場合には著しくなる。

光軸のずれの問題を避ける方法として，分析線の近傍にある非共鳴線をバックグラウンド吸光の情報を与える参照線として用いる方法〔I 55〕もあるが，同時補正のためには分光器が二台必要であるし，波長の違いによる補正誤差は避けられない。

ゼーマン効果を利用したバックグラウンド吸光補正法 (Correction methods for background absorption using the Zeeman effect)

上に述べた二方法の欠点がない正確なバックグラウンド吸光補正法として最近，ゼーマン効果を利用する原子吸光分光法が研究され実用化されてきた。ゼーマン効果の原子吸光分光法への応用は最初に Prugger らにより提唱され〔I 56〕，Hadeishi らにより装置が開発され研究が行われた〔I57〕。その後，Stephens ら〔I 58〕，内田ら〔I 59〕，小泉ら〔I 60〕，Grassam ら〔I 61〕により種々の基礎的検討が行われた。特に小泉らの研究，開発はゼーマン原子吸光分光法の実用化に大きく寄与した。ゼーマン原子吸光分光法も，原子吸光分光法や原子けい光分光法がそうであったように，古くに発見された現象（ゼーマン効果：1896年に Zeeman により発見される〔I 62〕）が長い年月を経てから実用面に応用された場合に該当する。また，ゼーマン原子吸光分光法の出現は，本論文の主題の一つである原子磁気旋光分光法をも含め，後に続く磁気光学効果を用いたコヒーレント分光法の開花をもたらすトリガーになるかもしれない。

ゼーマン原子吸光分光法にもいろいろあって，現在までに大きく分けて四種類の光学配置が報告されている。Hadeishi らにより報告された最初のものは〔I 57〕，異なった同位体を含むランプに光軸に平行な方向で磁場をかけ同位体の一方から出る σ 成分を原子吸光の，他方の同位体から出る σ 成分をバックグラウンド吸光の光源光として用いたもので，前者の吸光度から後者の吸光度を減じて正味の原子吸光の吸光度を得る〔I 57〕。この方法には波長シフトが適当な同位体が必要だという欠点がある。これに対し内田らによって提案された方法は，原子化器中の原子蒸気に光軸と平行な方向で交流磁場をかけ，吸収線の分裂で生じた σ 成分の波長を吸収線の波長の両側で変調し，生ずる交流成分を取り出す方法である〔I 59〕。バックグラウンド吸光は直流成分であるのでロックインアンプで除去できる。この方法には変調率の大きい交流磁場が感度を得るには必要である，吸収線プロフィルの歪が検量線の直線性を悪くするなどの欠点があるが，同位体を含み磁場中で安定に点灯する特別のランプを必要としない，偏光プリズムを必要としない，他の方法程には強い磁場を必要としないなどの特長がある。

上記の二つの方法はいずれも光軸に平行な方向に磁場をかけσ成分だけを利用する方法であるが，小泉らは光軸に垂直方向でランプに磁場をかけ生ずるσとπ成分をそれぞれバックグラウンド吸光と原子吸光用の光源に用いる方法を考案した〔I 60〕。偏光プリズムでσとπの成分を交互に取り出し後者の吸光度から前者の吸光度を減じてバックグラウンド吸光の補正を行う。また，光軸に垂直な方向で原子化器に磁場をかける方法をも考案した〔I 63〕。光源光の光を回転偏光プリズムで回転平面偏光としておくと，偏光面が磁力線に平行になったとき原子吸光が起こり，垂直になったときはバックグラウンド吸光のみが起こることを利用している。これらの二つの方法は，同位体を必要としない，静磁場を利用しているので永久磁石を使うことができるなどの特長がある。特に後者の特長は装置を小型，軽量にする上で重要である。現在，これらの二つの方法によるゼーマン原子吸光分析計のみが市販されているが，上記のことがその原因の一つであるかもしれない。二つの方法のうち，前者の方法による市販品は水銀専用であり，いろいろな元素に使うことのできる装置は後者の方法によるものである。このことの最大の理由には，原子吸光分光計用として一般に市販されている中空陰極ランプは磁場中でローレンツ力を受け放電が安定に点灯しないため，EDLのような不安定な光源を使わざるを得ないということがある。しかし，一方，後者の方法では多量の熱を発する原子化器を磁石の中に置かなくてはならないため，使える原子化器の大きさや種類に制約があるという欠点がある。この点では前者の方法の方が好ましい。高周波点灯した中空陰極ランプは磁場中で消えないことを利用しゼーマン原子吸光分光法の光源に供した例もあり〔I 121〕前者の方法による水銀以外の元素の分析のための汎用機が市販される可能性もある。

バックグラウンド発光補正法 (Correction methods for background emission)

原子発光分光法におけるバックグラウンド発光の分光学的な補正法は本質的には観測対象の原子スペクトル線の波長の両側の波長でのバックグラウンド発光を観測し，それを，原子スペクトル線の発光強度から差し引くという方法に基いている。このことを自動的に行う方法としては，次のようなものがある。分光器の入射スリットの直後に振動する石英板を置き，回折格子への入射角をわずかに振らすことにより，スペクトル線の両側のバックグラウンド発光を取り込み補正する方法。パルスモーターで回折格子の角度をかえるシーケンシャルスルースキャン（SSS）〔I 65〕の方法で，パルスモーターをコンピューターでコントロールしてスペクトル線と両側のバックグラウンド発光の強度を取り込みバックグラウンド発光をさし引く方法。回折格子は固定しておき，検出器にホトダイオードアレイ，ビジコン，シリコンインテンシファイドターゲット（SIT）〔I 66〕などのイメージセンサーを用いてSSSと同じ目的を果たす方法などである。いずれの方法を用いても原子発光分光法では分光系の分解能がバックグラウンド発光の正確な補正には不可欠である。特にNOのγバンドのような複雑に変化する分子スペクトルがバックグラウンド発光として原子スペクトル線に重なっている場合には，分光系の高い分解能が必要となる。

原子けい光分光法におけるバックグラウンド散乱補正法 (Correction methods for background scattering in AFS)

原子けい光分光法におけるバックグラウンド散乱の分光学的補正法としては上記の原子発光分光

法用の方法が適用できる。しかし，原子けい光分光法の特長は原理のところで述べたように高い分解能の分光器を必要としないことであるので上記の方法ではこの特長が生かされない。この特長を生かすと思われる方法として，原子吸光分光法で用いられている重水素放電管法を原子けい光法に応用した例[I 67]もあるが，以下に述べるような方法が示唆されている以外は決定的な方法は報告されていない。色素レーザーを光源として用いればストークス線とアンチストークス線も十分な強さで輻射されるので分析線として使うことができる。これらの線の波長は光源であるレーザー光の波長とは異なるのでバックグラウンド散乱は分光器により除去できる[I 23]。ゼーマン効果を原子けい光分光法に応用することは小泉ら[I 68]や Van Loon[I 23]によって示唆されているが，具体的な光学配置や実験については詳しい報告がない。その他に利用できる方法としては，レーザーけい光光度法で用いられている[1]次のような方法がある。バックグラウンド散乱は光源からの光子とMie散乱粒子の間での弾性散乱の結果により生ずるのに対しけい光は非弾性散乱により生ずる。その結果，後者は前者より時間的に遅れて輻射される。これを利用してボックスカーインテグレーターでそれぞれを別々にとり出すことができる。この方法は原子けい光分光法にも応用できると思われるが，バックグラウンド散乱光と原子けい光の間での輻射の時間差がけい光光度法の場合に比べ非常に短い（数〜数十 p秒のオーダー）ことから，特殊な超高速のボックスカーインテグレーターが必要であることが難点であろう。

干渉補正法 (Correction method for interference)

バックグラウンド信号の分光学的補正法を上に述べてきたが，もう一つの問題，即ち，試料マトリックスによる干渉の分光学的な補正は今までのところ報告されていない。

11. 本論文の主題 (Main subjects of the present dissertation)

この節では本論文の主題の位置付けを前節までの内容に関連付けて行う。本論文の主題は冒頭でも述べたように大きく二つに分かれている。一つは原子ファラデー効果を利用した原子磁気旋光分光法であり，他の一つは複数の原子スペクトル線を利用する多線法に関するものでそれぞれ本論文の第一章と第二章に記述してある。

原子磁気旋光分光法の意義と特徴 (Significance and features of AMORS)

原子磁気旋光分光法は前節の表5で分類すると，化学的な前処理を行わずに試料を直接原子化し，生ずるバックグラウンド散乱光を分光学的に除去する方法である。原子けい光分光法では有機物などのマトリックスを含む試料の原子化の際に生ずるバックグラウンド散乱が大きな問題でありこの方法の実用化を妨げる一因ではないかということを第7節で論じたが，原子磁気施光分光法には問題のバックグラウンド散乱光を原理的に除去できる能力がある。このことは，本質的には本法が光のコーヒーレンス性を利用していることに基いている。偏光が原子により選択的に旋光し，煙などのバックグラウンド散乱を引き起こす成分では偏光面がほとんど回転しないため第二の偏光子（検光子）により散乱光が除去できる。本法にはもう一つ重要な特長がある。それもやはりコヒーレ

ンス性に基くものであるが，原子けい光分光法と異なり，光源光の進む方向で観測するため光の回収率が高いことである。このため，原子けい光分光法のように強い光を出す無電極放電管のような特別なランプを使わなくても，原子吸光分光法として色々な元素に渡って広く市販されている中空陰極ランプを用いて実用的な感度が得られる。また，原子吸光分光法との比較においては，原子磁気旋光法が原子けい光分光法と似かよった特徴を持つので次のことが利点に挙げられる。

(1) 光源光の変動がベースラインの変動として現れない。

(2) 光源光強度に比例した感度が得られる。

(3) 光源光と試料から発生した原子蒸気が光源光と共鳴し，それ自身が分光器として働くため分解能が高い分光器を必要としない（非分散系も可能）。

(4) 連続光源を使えば多元素同時分析も可能である。

原子磁気旋光法では大部分，旋光という物理量を測定している。（Kersey ら[I 75] によれば磁場強度の低いところでは円偏光二色性による楕円偏光も一部寄与している）したがって，自然放出による発光を測定している原子発光，吸光量を測定している原子吸光分光法，けい光量を測定している原子けい光分光法のいずれにも分類できない新しい方法である。

ところで，原子磁気旋光法が原子けい光分光法で問題となるバックグラウンド散乱を除去できる方法であることは，ゼーマン原子吸光分光法が通常の原子吸光分光法で問題となるバックグラウンド吸光を補正し除くことができる方法であるという関係に似ている。また，原子磁気旋光分光法が利用しているファラデー効果はゼーマン効果の結果として生ずるものであることから，見方によっては，原子磁気旋光分光法はゼーマン原子吸光分光法と共に磁気光学効果の原子分光法への応用という範疇に入れることができるとも考えられる。この点をもう少し検討するために，第7節において従来の原子分光法について行ったように，歴史的背景を原子ファラデー効果についてもたどってみよう。

ファラデー効果とフォークト効果の研究史(Research history of the Faraday and Voigt effects)

磁場をかけた物質中で光の偏光面が回転するという磁気旋光の効果，即ちファラデー効果は，1846年に Faraday が鉛ガラスについて発見した[I 69]。その後，Faraday，Wiedeman，Verdet らにより研究が行われ，1800年代の終りまでには水，石英，水素分子，酸素分子などの種々の物質についてファラデー効果が観測された。現在においても，分子のファラデー効果は磁気旋光分散法[38]として，光学活性がないため旋光分散法では測定ができない有機化合物の分析法として注目を集めつつある。しかし，まだ広くは応用されていない。

ファラデー効果が何故起こるのかが説明されるには，Faraday による発見後，半世紀余経過してゼーマン効果が発見されるまで待たなくてはならなかった。1896年，Zeeman は磁場中にある原子から放出されるスペクトル線が複数に分かれることを発見した[I 62]。因に彼はこの現象を恩師である Lorentz の電子論を応用して説明した。こうして電子の存在の実験的証明を行ったのである。Zeeman と Lorentz は共に1902年，この業績でノーベル賞を受賞した。

そのすぐ後の1898年に原子のファラデー効果が Macaluso と Corbino らにより「磁場中の金属蒸気を通る光によって生ずる新しい作用について」という論文中で報告された[32]。偏向面が直交したニコルプリズムの間に，電磁石で磁場を光の進行方向と平行に印加したブンゼンバーナーを置き，炎の中にナトリウム蒸気を発生させたところ，光源光に太陽光という白色光を使っているのにナトリウムD線の黄色の光が観測されたのである。しかも，磁場の強度を変化させるとその光が強くなったり弱くなったりした。彼ら自身はこの効果をうまく説明できなかったが，この報告とほとんど時を同じくして，Voigt が理論的解釈を与えた[I 70]。それによるとファラデー効果は二年前に発見されたゼーマン効果により生ずる二つの σ 成分による複屈折の結果生ずる施光に基くものである。σ 成分は偏光面が円運動をしているのでファラデー効果は磁気円偏光複屈折とも言える。

Voigt の理論は複屈折が磁場の方向と垂直な方向に進む光でも起こることを予言していた。その直後の1899年，Cotton はこの効果をナトリウムの原子蒸気について実験的に確認した[I 71]。後に Cotton と Mouton はニトロベンゼンについてもこの効果を報告している。このことから，この効果はフォークト効果ともコットン－ムートン効果とも呼ばれている。また，この効果は観測方向では平面運動をしている σ と π 成分による複屈折の結果生ずるものであるので磁気平面偏光複屈折とも言える。1930年代の初頭までには結晶，溶液，有機化合物などのフォークト効果について多くの報告がなされた。ファラデー効果と同様に現在において分子のフォークト効果は旋光分散法を補う方法として利用されつつあるが応用はまだ比較的少ない。

1930年代に入ると量子力学が急速に発達しつつある中で原子スペクトルの微細構造や，超微細構造，ハンレ効果などの理論的解釈が進んだが，ゼーマン効果も量子力学によって理論的裏付けが行われた。従って，ゼーマン効果と関係のあるファラデー効果やフォークト効果の理論的解釈も必然的に進行したが，原子蒸気についてのこれらの効果の実験的観測はブンゼンバーナー中またはステンレス加熱管中のナトリウムの蒸気とグロー放電中の水素原子[33]に限られており，他の元素についてはほとんど報告がない。この原因は不明であるが，物理学者の興味がファラデーやフォークト効果という効果自体にあったので生成しやすいナトリウムなどの系を用いて効果自体を調べた後は，他の蒸気圧の低い元素について原子化方法で苦労してまでも調べようという興味が生じなかったのかもしれない。

戦後の物理学における原子磁気光学効果に関する研究の流れ (Research interest in atomic magneto-optical effects in physics after War)

第二次大戦後，物理学の原子スペクトルの領域においては，複雑な超微細構造や同位体シフトに対しての関心が増加した。1950年代から1960年代にかけて，Bitter，Corney，Series，Dodd，Kastler らは超微細構造や同位体シフトを調べる新しい方法として磁気光学二重共鳴法，磁気摂動けい光分光法，光ポンピング法などの磁気光学的な新しい方法を開発し研究した。Kastler はノーベル賞を受賞している。以上の方法はいずれもゼーマン効果を介して核磁気共鳴分光法，電子スピン共鳴分光法，レーザー磁気共鳴分光法などの磁気共鳴法と深く関係しており，これらの方法の研究開発の流れの影響を受けている。

こうした物理学における原子スペクトルの研究の新しい流れの中で，原子のファラデー効果とフォークト効果も原子スペクトルの超微細構造や同位体シフトを調べる方法として利用できることが，1966年に Corney らによって報告された[34]。彼らは水銀の253.65 nm の共鳴線を調べる研究の中で，この方法が原子けい光分光法と違い前方で光を観測するためコヒーレンス性があるという特長を挙げている。彼らは，ファラデー効果とフォークト効果を前方散乱と呼び，詳しい理論を展開している。（光子と物質との相互作用の結果，出てくる光子は広い意味で散乱といってよい。例えば原子けい光は原子非弾性横方向散乱とも言える。）Hackett らはこのコヒーレンス性を利用して水銀の共鳴線（253.65nm）中で起こる $\sigma-\sigma$ 間の線交叉を観測し，超微細構造と同位体シフトを研究した。[35]

原子磁気効果の分析化学への応用の開始 (Commencement of application of atomic magneto—optical effects to analytical chemistry)

前節で述べたゼーマン原子吸光分光法の先駆者の一人である Hadeishi も HgI 253.65nm中の超微細構造の研究を前方散乱の方法を用いて行っていた。その研究の中で，1974年，彼は前方散乱法が空気中の微量水銀の検出に利用できることを示した[36]。おそらくこれが前方散乱法を原子分光分析へ導入した最初のものであろう。1977年，著者ら[I 72]と Ito ら[I 73]はそれぞれファラデー効果とフォークト効果利用した原子分光法をカドミウムについて示し，電気加熱原子化器を用いた実用的な装置の開発を始めた。その後，やはりゼーマン原子吸光分光法の先駆者の一人である Stephens もファラデー効果を空気中の水銀の検出に応用した[44]。

ファラデー効果とフォークト効果を利用した原子分光法は，1800年代後半における効果自体に対する研究経過は異るにしても，上記からわかるように分析化学への応用はよく似た研究土壌から派生してきていると見ることもできる。中には，原理的にもゼーマン原子吸光分光法自体から派生したものと位置付けた報告もある[I 122]。しかし，著者ら，Murayama ら，Stephens らの初期の研究において既に，ファラデー効果やフォークト効果を用いた原子分光法は原理的に原子発光，けい光，吸光分光法とは異なり，（従ってゼーマン原子吸光分光法とも異なり，）分析化学的にもこの節の初めに述べたような特異的な特徴があることが示された。

現在では，著者らがファラデー効果を利用した原子分光法（原子磁気旋光分光法）を，Ito ら[I 73]，Stephens[44]，Kerseyら[I 75]，Hirokawa ら[I 76]，Dubuset ら[I 77]がフォークト効果を用いた原子分光法を研究しているのみでまだ研究者の数も少い。しかし，最近になって，これら研究者によって，二つの方法について色々な研究が開始された。二つの方法の特徴の一つである，光源光に比例して検出光が強くなることから，高周波駆動した中空陰極ランプ[I 78]，パルス駆動した中空陰極ランプ[I 79]，グリムランプ[80]などの高輝度の光源を用いて感度をさらに上げようとする試み。試料からの原子自体が分光器になる性質から，キセノン白色光源を用いて多元素分析を行おうとする試み[I 77]。種々の元素の共鳴線のゼーマン分裂パターンと旋光強度の磁場依存性の調査[I 123]。検量線の直線化[I 81]。電気加熱原子化器中の原子分布測定への応用[I 82]など。これらの研究を通して，原子磁気旋光分光法とフォークト効果を利用した原子分光法はいくつ

かの元素について原子吸光分光法に匹敵する感度（例えばカドミウムではsub pg ）を与えることがわかってきた。

原子磁気旋光分光法は普及するか？ (AMORS — pervades ?)

このように種々の研究が行われつつあるが，表１－２でいうとまだ第１または第２段階であり，はたしてこれらの方法は原子吸光分光分析やICP発光分光分析のような実用的な方法として普及するであろうか。これを予測することは，初めの方の節で議論したように，複雑な因子のためかなりむつかしいと思われる。しかし，バックグラウンド信号の光学的な除去という点で共通点を持っており，比較的に速い普及をみたゼーマン原子吸光分光法を参照するとわかり易いかもしれない。

表３に掲げた原子分光分析の歴史からも分るように，ゼーマン原子吸光分光法が装置化された時期には原子吸光分光法自体は分析法として安定期にあり，原子化器や光源などの必需技術および実際分析に関連したソフトウェア（応用例，試料処理方法，サンプリング法等／一種のクッキングブック）が十分に吟味されていた。このような状況において，関連技術とソフトウェアをほぼそのままに使えるゼーマン原子吸光分光法は応用分野のユーザーに比較的すんなり受け入れられたのかもしれない。

原子磁気旋光分光法はどうであろうか。この方法も光源としては原子けい光分光法のように無電極放電管を使わなくても，広く普及している原子吸光分光法用の中空陰極ランプを使って実用的な感度が得られるし，原子化器も原子吸光分光法用のものが使える。また，原子吸光分光法に比較して分光器の分解能ははるかに低くてよい。さらに，磁場強度もゼーマン原子吸光分光法に比べると低くてよい（～数 kG）。これらを考えると本法が実用的な方法として普及する可能性はあると思われる。特に，分解能の低い小さな分光器と小さな永久磁石が使えるので装置の小型軽量化が可能だと思われる。現在，著者らは車のバッテリーで作動する約 60×40×20 *cm*，15 *kg* の車搭載用の装置を開発中である。この装置は，前にも述べたが，海洋調査や，内陸における鉱物資源や土地開発における環境評価などの様にサンプリングしてから研究所まで持って行くのに日数がかかる場合の現場分析，重金属廃液の不法投棄を現行チェックするための現場における迅速分析などに応用できるものと思われる。これらの現場分析の場合には，湿式灰化などの複雑な化学的前処理は困難であるし，迅速性を要求されるために直接分析が不可欠となるが，原子磁気旋光分光法のバックグラウンド信号除去能力はこの目的に合っている。

第１章の概要 (Abstract of Chapter 1)

さて，この論文の本論第１章には「原子磁気施光分光法」が述べてある。第１章は1－1から1－7までの節に分かれており，１－７の付録を除いて，各節にはそれぞれ冒頭にその節の内容についての背景に関する小序文が，末尾にはその段階での小結論が書かれている。以下に各節の内容の流れを簡単に述べる。

１－１～１－６節の内容の流れは，原理，その原理が分析法として応用できるかどうかの実験的な確認，光学系，電子回路を含む装置化における最適化，いくらかの応用というようになっている。

この流れは，見方によっては，表１－２で示した一分析化学的方法の開発課程を縮少したものに似ていると言えるかもしれない。

１－１節では原子ファラデー効果の原理が述べられている。１－２節では関連する基本的な式とそれから予測される原子磁気旋光分光法の分析化学的な特徴を述べてある。これら二つの節は表１－２の第一段階に対応するであろう。

１－３節では原理が応用できるかどうかをまず大まかに調べるためにプロトタイプの装置を組み立て，それを使って Cd についてのファラデー効果を実験的に調べた結果を述べてある。その結果から原子磁気旋光分光法の特徴を前の理論的予測と比較している。Cd を選んだのは Cd が比較的原子化し易く，また，その分析線（228.8nm）の遷移確率が高く実験がやり易いことと，単純なゼーマン分裂パターンを示すため理論との比較がし易いためである。この節の実験はそれ以後の複雑なスペクトル構造を持つ他元素への応用に先立つ予備実験である。

１－４節では，超微細構造を持つ他の元素の原子ファラデー効果をも扱うことができるような理論の展開が行われている。摂動法の適用により複雑なゼーマン分裂パターンをコンピュータで計算しゼーマン成分間の線交叉を予測し，旋光強度の磁場強度依存性との関係を明らかにしている。実験的観測により Cu，Au，Bi，Cs などについて線交叉を観測し，計算結果との照合を行っている。これらの元素についての線交叉は物理分野でも報告されていない。原子化しにくい元素を再現性よく原子化できる装置が存在して初めてこの種の観測が行われる。このように，物理学的に興味があっても分析化学的な研究において開発された技術がないと観測しにくいような現象もある。得られた結果は物理学での解釈に役立つ場合もある。（図１で論じた分析化学からそのベースの一つである物理学へのフィードバック。）また，この節では原子磁気旋光分光法の他の重要なパラメータ，即ち，旋光強度の光源光強度への依存性，二乗特性の検量関係などを種々の元素について検討している。この節までは表１－２の第二段階までに対応するものと考えてもよいであろう。

１－５節には光源としてパルス駆動した中空陰極ランプを用いる方法が述べられている。１－４節までの節で，理論的にも実験的にも原子磁気旋光分光法では光源光を強くすると感度が向上することが分ったため，中空陰極ランプに瞬間的に大電流を流し光源光強度の増大を試みている。パルス駆動時の分光学的基礎特性をも検討している。

１－６節では試料の直接原子化による分析に適合するように原子磁気旋光計の改良を行っている。原子磁気旋光分光法ではこの節の初めの方で述べているように，試料の原子化の際に生ずる煙などによるバックグラウンド散乱は除去できるが，バックグラウンド吸光により旋光強度が減衰し負の光学的干渉を与えるのでこれを補正する光学系を組み立てている。この光学系は，同時に原子吸光による旋光強度の減衰に起因する負の光学干渉と光源光強度の変動による旋光強度のゆらぎをも補正できる。補正のためのいくつかの光学系を試作しそれらの性能をチェックして，最適な光学系を決定している。これらの内容はハードウェアの最適化であり，表１－２の第三段階に対応するものと思われる。

この節の後半では，最適化された装置の機能を実際の試料でチェックするために，植物性，動物性，火山灰マトリックスなどの標準試料を直接原子化することにより分析し，精度や正確さなどを調べている。研究室間チェックも一部の試料については行っている。これらの内容は部分的には表1－2の第四段階（応用）に対応していると考えてもよいであろう。

表1－2でも説明したように，応用段階に入って障害が生じた場合，前段階に，場合によっては第一段階に戻る（フィードバックする）必要が出て来るし，他の方法との組み合わせの必要性も生ずる。これらについての具体的なことは巻末の総括で述べる。

また，上で述べた各段階の推移はこの節の前で述べたように，あくまで本論文における一つのミニチュアモデルであり，表1－2でいうところの方法論の大きな流れそのものではないので，大きな流れの中での原子磁気旋光法の評価は幅広い応用を待たなくてはならないであろう。その段階で新たなフィードバックが生ずるものと思われる。

多線法の意義 (Significance of Multi—line method)

本論文のもう一つの主題，「多線法」は表5の分類では，干渉の分光学的補正法に当る。試料マトリックスにより，原子化器または励起源で生ずる干渉現象は通常，前処理により分離して除くが，本法は生ずる干渉を分光学的な情報から補正する方法であり，前節において表5に関して論じたように今までのところ他に報告されていない。多線法は干渉の機構解明（メカニズムリサーチ)にも有用な情報を与える。もともと著者にとって多線法の研究は干渉の機構解明への興味から出発しているので，このことは当然のことと言ってもよいであろう。

機構解明の重要性 (Significance of mechanism research)

機構解明は，物理学，物理化学などにおいてはもちろん，最重要の研究内容である場合が多く議論の余地はないと思うが，分析化学（特に機器分析）において，機構解明がどのような意味を持つかはあまり議論されてないし，また，本論文の第二主題である多線法を前に述べた一般論に関連付けて位置付ける上でも必要であるので以下に述べる。

機構解明は図1においては分析化学の科学的ベースに当たると思われるが，表1－2でいうと第一段階（方法の原理，理論）とは違いむしろ第四段階の応用から第一段階へのフィードバックに相当するものと考えられる。応用が進んだ段階において第三段階のハードウェアの改良や，異った方法の結合のみでは解決できないような問題が残った場合などに，その原因をなす機構の解明が必要となる。機構が解明された段階でそれを解決する方法を第一段階の原理に立ち戻って考える。このような経路で新しい方法が生まれる場合がよくある。

機構解明の重要性についてはいくらかの人が指摘している。例えば Barnes〔I 10〕は ICP についての総説の中で ICP の将来の研究方向の一つに ICP の機構解明があることを指摘している。Sturgion らもまた，電気加熱原子化器の新たな開発のためには原子化機構の解明が重要であることを強調している〔I 83〕。

さて，機構解明で第一に重要なのは関係している物理量をいかに独立的にかつ定量的に決定する

かということであろう。このことを原子化器や励起源中の機構解明の研究について考えてみる。

機構解明における推定 (Deduction in mechanism research)

今までに原子化器中で生ずる化学干渉については数多くの研究が報告されている。しかし，それらの多くは一種類の情報，即ち具体的には原子吸光または吸光度という量の変化のみからの推定によるものである。典型的な例として空気－アセチレン炎中でMgの原子吸光はAlが共存していると負の化学干渉を受けることが知られており，これは両元素の酸化物の原子化が耐火性の複合酸化物の生成により抑制されることに起因していると考えられている。しかし，関係する自由原子も含めた化学種の数の変化をすべて追跡した訳ではなく，ただAlの添加に対するMgの吸光度の減少のみからの推定である。このような推定は空気－アセチレン炎中のCrとFe間相互でみられる複雑な化学干渉[105]の場合には適用し難い。また，電気加熱原子化器の場合には，その上，時間的変化を伴うため推定はさらに困難となる。

したがって，関係する化学種の数の変化を追跡することが化学干渉を解明する上で重要となるが，問題は観測できる分光学的情報（原子吸光分光法では吸光度，原子発光分光法では発光強度，原子けい光分光法ではけい光強度）が直接的に原子の数を反映していないことである。原子化率，励起温度，イオン化率などの因子が複雑に影響する。

励起温度 (Excitation temperature)

アーク，スパーク励起源の研究においては励起温度の重要性は割合に早くから気付かれておりプラズマのキャラクタリゼーションに用いられていた。励起温度を最初に測定したのはOrnsteinら[I 84]で，上のエネルギー準位が異なる二本の原子発光線の強度を比較する方法を取った。この方法は現在，Ornsteinの二線法として知られている。Gartonら[I 85]は，この方法をボルツマンプロットする方法に拡張しアークプラズマ中の原子の励起温度を測定した。Corlissら[I 86, I 87]は77元素の発光線について遷移確率の表を作った。遷移確率は上記の方法においては不可欠なものである。それ以来，種々のプラズマや化学炎中の励起温度が測定されるようになった。

原子吸光のモードで励起温度を二線法により測定する方法を初めて導入したのは電気加熱原子化器で有名な（表3参照）L′vovであった[I 88]。それ以後，電気加熱原子化器中の無輻射原子の励起温度についての報告がいくつかなされ[I 89, I 90]，原子化におけるエネルギー移動の理解の一助となった。

時間的変化を含めた研究 (Study involving transient change)

前に述べたように，電気化熱原子化器における原子化機構には時間というパラメータが重要な役割をする。このような観点から，Matousek[I 91]とAdamsら[I 92]は電気加熱原子化器中のNi原子の励起温度の時間的変化を調べた。Sturgionら[I 83]も同様にして電気加熱原子化器表面から生成原子へのエネルギー移動の過渡的変化を研究している。

時間を解析因子として含めた電気加熱原子化器中の原子化の研究には，その他にも次のようなものがある。Yanagisawa[I 93]はガラス状炭素原子化器におけるSrの原子化においてAr（＋

不純物の O_2 ）を雰囲気ガスとして用いた場合に原子吸光ピークが著しくテーリングすることを見い出した。SrO→Sr+O の反応を仮定し吸光ピークから計算したところ，値が SrO の解離エネルギーの 90 kcal ／ mol とほぼ一致した。H_2 を Ar に添加するとテーリングはなくなった。このような速度論的取扱いにより Sturgion ら〔I 83〕は種々の元素について原子化器の還元性を含めた原子化機構の研究を行った。その他にも原子の拡散係数も原子化機構を解釈するために必要な因子として測定されている〔I 94〕。

イオン化率と原子化率の測定方法 (Methods to determine degrees of atomization and ionization)

さて，話が時間を含む解析の方法へ逸れたが，化学炎やプラズマトーチなどのような定常状態で扱える系に話を戻そう。これら系についての機構解明において，励起温度以外の重要な因子はイオン化率と原子化率である。励起源では励起温度が高いためイオン化率の方がどちらかというと支配的な因子である。Corliss〔I 87〕はアークプラズマ中の種々の元素のイオン化率を原子発光線とイオン発光線の強度を比較して測定した。一方，原子吸光分光法に用いられるような原子化器では励起温度は励起源に比べ低い（～3000 K）のでアルカリ，アルカリ土類元素以外の元素についてはイオン化率よりも原子化率の方が支配的な因子と思われる。De Galan〔I 95〕はいくつかの元素について化学炎中の原子化率を測定した。彼らの方法は Cu の化合物が化学炎中でほぼ完全に原子化する，即ち原子化率が 1 だと仮定し，原子吸光度比から相対原子化率を求める方法で，最初の仮定にやや問題があった。

Manning ら〔I 96〕は，イオン化率を求める別な方法を報告している。原子線とイオン線の吸光度をイオン化干渉が起きている場合と起きていない場合について測定し連立方程式を解く方法で二つの場合のイオン化率を求めることができる。同じ考え方で，原子線の吸光度と分子線の発光強度の変化から原子化率を求めた例もある〔I 97〕。これらの方法は簡単な手順で干渉におけるイオン化率や原子化率の変化を求められる長所はあるが，原子やイオンの励起温度とそれらの総数が一定であるという仮定を含んでおり，広く応用するには難点があった。

イオン化率を求める方法として最初に述べた Corliss の方法は De Galan らや Manning らの方法に含まれるようなタイプの仮定がないという特長を持っている。しかし，やはり，別の仮定，即ち原子とイオンの励起温度が同じであることとそれらの関数である分配関数が一定であるということを含んでいる。このような仮定は原子化器や励起源の特性を知る上で大きな誤差を与えることが多いと思われる。

原子やイオンの励起系の分配関数については Corliss 以後は正確な関数を報告しているものがなかったが，1968年に De Galan がほとんどの元素の原子，イオンについての分配関数をテーラー級数の形で与えた〔92〕。（残念ながら De Galan の分配関数はその後あまり利用されていないが。）

干渉機構解明法としての多線法とその特徴 (Multi－line method as a method for mechanism research and its features)

さて，本論文の主題である多線法は，De Galan の分配関数を使い原子およびイオンの励起温度，イオン化率，原子化率を別々に独立して測定値から求める新しい方法である。励起項のエネルギー

の大きさが異なる遷移から生ずる二本の原子発光線の強度を比較し原子の励起温度を求める（Ornsteinの二線法）。同様に二本の異なるイオン発光線を使いイオンの励起温度を求める。次に原子発光線とイオン発光線の強度と前で求めた二つの励起温度を使い，De Galanの分配関数を含む式によりイオン化率を求める。イオン線の代わりに分子発光線を用いれば原子化率が同様にして求まる。もし，励起項のエネルギーが異なる遷移から生ずる発光線が三本以上観測できればボルツマンプロットから励起温度が求まる（この方がボルツマン分布に系が従っているかどうかということがわかるし，精度もよいが，系の励起温度が低い場合には実際には利用できる発光線は少ない場合が多い。）

多線法は，また，吸光モードにも適用できる。電気加熱原子化器において温度が低い場合においては発光を観測することは困難であるので吸光モードの多線法が適している。

多線法の主な特長を以下にまとめる。

(1) Corliss，De Galanら，Manningらの方法で問題となった仮定を必要としない。

(2) 原子およびイオンの励起温度，イオン化率，原子化率が独立に求まり，かつこれらの因子は直接的にスペクトル線強度の変化に関係づけられているので観測した干渉現象との対応がつけやすい。

(2)の因子のどれかの大きさが干渉現象で変化すればそれを基にその因子を変化させる機構を考えることができる。例えば原子発光線強度に対し負の干渉があったとき原子の励起温度のみが下がったとすると，マトリックスが加わることによる励起原子の失活が生じている，というように的確に判断できる。

さて，原子およびイオンの励起温度，イオン化率，原子化率が独立に求まると，次に，これらの因子と，もともとの情報源としてのスペクトル線の強度とから原子やイオンや分子などの，励起源や原子化器中での機構に関係している化学種の数（相対数）が決定できる。これらの情報も干渉機構の解明に役立つ。

干渉補正法としての多線法 (Multi — line method as a method for interference correction)

以上に多線法の機構解明における意味を述べたが，最初に述べたように多線法のもう一つの目的は干渉の分光学的補正である。機構解明の方法を補正法という一つの分析化学的方法にすることは，表1－2で言うと機構解明というフィードバックの過程を通して第一段階に戻り，方法の原理の構築（発案）をすることに対応すると考えられる。

原子，イオン，分子などの数が決められると，それから，それらの総数，即ち分析目的元素を含む化学種の総数が決まる。この総数は励起源や原子化器の内部で生ずる干渉（化学干渉，イオン化干渉，励起干渉）に関係なく最初に導入された量に対応して一定の値である。したがって，この総数をスペクトル線強度の代わりに用いれば干渉に影響されない分析を行うことができる。これが，多線法による干渉補正法のエッセンスである。別な見方をすれば，励起源や原子化器からは複数の原子スペクトル線が出ており，多くの情報を含んでいるにもかかわらず，今までの原子分光分析では，ほとんどの場合，一本のスペクトル線の強度のみが検量や分析における情報として使われてい

たわけで，多線法は今まで取り込んでいなかった情報を捕える一つの方法であると言える。

多線法は，感度は高いが励起やイオン化過程での干渉に悩まされるMIPにおける干渉補正に有効だと思われる。また，干渉が少ないICPにおいても，多元素同時分析において全元素にわたり干渉が少ないプラズマ観測領域を設定しにくい（プラズマガスなどの流量条件によっては）などの場合に，多線法は干渉による正確さの低下を防ぐのに役立つものと思われる。

第2章の概要 (Abstract of Chapter 2)

この論文の本論第2章に「多線法」が述べてある。第2章は2－1から2－4までの節に分かれており，第1章の場合と同様に，各節の冒頭には小序文が，末尾に小結論が付されているが，以下に各節の内容の流れを簡単に述べる。

第2章の冒頭には干渉について幾らか詳しく，具体的な励起源や原子化器と関連付けて論じている。（この部分は本序文の干渉の記述と重複するところもあるが，多線法で重要な因子として取り扱われる励起温度，イオン化率，原子化率にさらに直接的に関連付けて論じている。）

2－1節には上記の内容を受けて，励起源や原子化器の中で生じている過程（原子化や励起，イオン化過程を含む）を単純化したモデルを考え，それをもとに種々の励起源や原子化器に適用できる多線法の一般式を導いている。即ち，この節では多線法の理論的背景を述べている。2－2以後の節ではこの節で導かれた一般式をもとに各節で取り扱う特定の励起源や原子化器，また，観測するスペクトル線に応じて変形した式を導き，用いている。

2－2節では多線法を励起源の一つであるCMPに適用している。CMPでは種々の元素について顕著な元素間干渉がみられた。これは，主に原子の励起とイオン化の過程，およびイオンの励起の過程に関係していると予測された。そこで，原子発光線とイオン発光線が明確に観測されたMnをモデルとして取り上げた。多線法により，CMP中の励起温度とイオン化率の空間分布を調べることにより，プラズマの基本的特性を検討した。（2－2－1～2－2－3分節）次に，干渉の機構を調べるために，イオン化し易いアルカリ金属やアルカリ土類金属元素を干渉剤のモデルとして共存させ，Mnについて励起温度やイオン化率の変動を調べた。このことにより干渉機構にこれらの因子の変動が大きく関係していることを指摘する。また，ICPについて報告されている干渉現象とも関連付けて論ずる。さらには，Mnについての結果をもとに，他の元素における共存元素効果についても論ずる。（2－2－4分節）

この分節の最後では，多線法による干渉の補正例をMnについて示している。干渉補正が成立するためにはプラズマの空間的対称性が重要であることを指摘している。

2－3節では多線法を化学炎を用いた原子化器に適用している。2－2節のプラズマの場合には励起温度とイオン化率を支配的な因子として取り扱っているが，本節で扱う化学炎の場合は，原子化機構と化学干渉の解明を目的として，励起温度と原子化率を支配的な因子として取り扱っている。

2－3－1分節では多線法を空気－水素炎中での銅の塩化物の原子化挙動の研究に応用している。この結果から，原子化率に対し支配的に影響する因子は炎の温度でなくて，炎の還元雰囲気である

ことを指摘している。

2－3－2分節では多線法を空気－アセチレン炎中でみられる Cr と Fe 間の複雑な化学干渉機構の解明に応用している。Fe, Cr の原子発光スペクトル以外に FeO, CrO の分子発光スペクトルが支配的に強いものとして観測されたので，これらのスペクトル線強度から励起温度，原子化率および原子，分子の総数を算出している。これらの因子の変化をもとに，炎の還元性が原子化に重要な働きをしていることを指摘している。また，Cr と Fe 間の化学干渉が，FeO と CrO の複合耐火物の生成，O 原子の移動などの現象に起因しており，それが炎の還元雰囲気の変化によって複雑に変化することを明らかにしている。

2－4節では多線法を電気加熱原子化器に適用している。

前にも述べたように，電気加熱原子化器では励起温度が低いために，その測定は原子吸光モードでなくては困難である。2－4－1分節では，その方法に関する式を誘導している。また，誘導した式を用いて，ガラス状炭素片を用いた原子化器におけるPb 原子の励起温度を測定している。その空間的分布と原子化器の温度との関係から，原子化器から Pb 原子への熱移動や，Pb 原子の失活の様子を明らかにしている。

1－4－2分節では，上で検討された方法を用いて，Ni，Sn，Pb の励起温度を測定し，それらの違いの原因を検討している。また，決定された励起温度と分子発光線を用いて，ガラス状炭素管原子化器中における銅の塩化物の原子化率を測定している。また，この原子化率の変化から雰囲気ガスに添加した水素の還元作用を物理的パラメータを用いた形で明らかにしている。

Abbreviations

AMORS; atomic magneto-optical rotation spectroscopy (metry)

AES; atomic emission spectroscopy (metry)

AAS; atomic absorption spectroscopy(metry)

AFS; atomic fluorescence spectroscopy (metry)

ICP; inductively coupled plasma

OES; optical emission spectroscopy

MIP; microwave-induced plasma

EDL; electrodeless discharge lamp

HCL; hollow cathode lamp

ETA; electrothermal atomizer

SIT; silicon intensified target tube

SSS; sequential slew scanning

IR; infrared

UV; ultraviolet

VUV; vacuum UV

NMR; nuclear magnetic resonance

ESR; electron spin resonance

ME; medical electronics (engineering)

CT; computer tomography

FT; Fourier transformation

GC; gas chromatography

LC; liquid chromatography

MS; mass spectrometry

ppm; parts per million

ppb; parts per billion

RF(rf); radio frequency

XFS; Xray fluorescence spectroscopy

PIXE; proton(particle)-induced Xray emission

EPMA; electron probe microanalysis

IIXMA; ion-induced Xray microanalysis

SSMS; spark source MS

IMMA; ion microprobe mass analyzer

SIMS; secondary ion MS

LAMMA; laser microprobe mass analyzer

EPA; Environmental Protection Agency

M.W.; molecular weight

CMP; capacitively coupled microwave plasma

PGC; pyrolysis GC

ZAAS; Zeeman AAS

ZAFS; Zeeman AFS

CFS; coherent forward scattering

MOR; magneto-optical rotation

MORD; magneto-optical rotatory dispersion

ORD; optical rotatory dispersion

LMR; laser magnetic resonance

hfs; hyperfine structure

LTE; local thermal equilibrium

IC; integrated circuit, ion chromatography

DTA; differential thermal analysis

DSC; differential scanning calorimetry

DC(dc); direct current

AC(ac); alternating current

VR; variable resistance

R.S.D.(r.s.d.); relative standard deviation

D.L.(DL); detection limit

S/N; signal to noise ratio

LSI; large scale integrated circuit

SSI; small scale integrated circuit

MSI; medium scale integrated circuit

Amp.; amplifier

A/D; analog to digital

D/A; digital to analog

MPX; multiplexer

S/H; sampling and holding

NF; negative feedback

CPU; central processing unit

MPU; microprocessing unit

I/O; input and output port

BPF; bandpass filter

LPF; low pass filter

RAM; random access memory

ROM; read only memory

ALU; arithmetic logical unit

NBS; National Bureau of Standards

O.L.; Orchard Leaves

Chapter 1

AMORS spectrometer

Chapter 1 ATOMIC MAGNETO-OPTICAL ROTATION SPECTROSCOPY

1-1 History and Principle

Atomic-fluorescence spectroscopy [10,29,30] has been developed as a useful technique for the determination of trace amount of elements. It requires no thermal excitation of atoms and consequently can reduce the known inter-element effects due to variations in the excitation temperature or the degree of ionization of atoms, that may be encountered in atomic-emission spectroscopy [31]. Compared with atomic-absorption spectroscopy, the noise in the light source does not contribute to the noise on the base line. Further, the intensity of the re-emitted radiation increases with increasing source intensity and the development of intense light sources may therefore enable the analytical sensitivity to be improved. As the re-emitted light has a very narrow band width, the construction of a non-dispersive detection system and multi-element detectors is feasible.

However, two problems in the practical application of atomic-fluorescence spectroscopy must be pointed out: the difficulty of collecting the re-emitted radiation necessitates the use of a sensitive detector, such as a photoelectron counter, and the background signal produced by scattering of the source radiation by non-atomic species produced in the atomizer, for example water droplets in a total consumption burner or smoke generated by pyrolysis of organic substances in the sample matrix in a furnace atomizer.

In this section, a spectroscopic method utilizing the Faraday effect is proposed for overcoming these problems. A magnetic field is applied to an electrothermal atomizer in the direction parallel to the propagation of the source radiation, as shown in Fig. 1. The electrothermal atomizer is located between two plane-polarizing prisms in a crossed configuration. When the atomic vapour is absent or not magnetized, the source radiation is blocked by the analyzer. Owing to the Faraday effect, the magnetized atomic vapour rotates the plane of polarization of the incident light, which then passes through the analyzer. By this means we can detect the presence of analyte atoms.

Macaluso and Corbino [32], in 1898, stated that a rotation of the plane of polarization was observed when a magnetic field was applied to sodium vapour. They employed solar light or an arc discharge as the source. A stainless-steel tube containing sodium metal was placed between crossed Nicol prisms and a magnetic field was applied by means of a solenoid coil. They heated the tube with a burner to vaporize the sodium metal and measured the angle of rotation by revolving the

Fig. 1. Schematic diagram of the Faraday configuration.

analyzer. They found that magnetic rotation occurred in the atomic vapour of sodium as well as in the molecular vapour of Na_2. Later, Ladenburg [33] discussed magnetic rotation by hydrogen atoms. More recently, Corney *et al.* [34] applied dispersion theory to this phenomenon and to the Voigt effect for atomic vapour. They called the phenomena "forward scattering of resonance radiation." Making use of the fact that the forward-scattered light is coherent, Hackett and

Series [35] studied the line-crossings (see under Principle) of the isotope-shifted lines in Hg I 253.65 nm. Church and Hadeishi [36] studied the line crossings and pointed out the possibility that the phenomenon was applicable to the trace determination of mercury vapour in air. The Faraday effect applied to molecular spectroscopy is called magneto-optical rotation (MOR), and is expected to be useful for the determination of molecules that are optically inactive and difficult to examine by optical rotatory dispersion. Buckingham and Stephens [37] described the theoretical aspects of MOR in detail. Although this principle has been used for the modulation of a laser beam, its development for analytical purposes has, to date, been limited. The Faraday effect applied to atomic spectroscopy can be called "atomic magneto-optical rotation" (AMOR).

The phenomenon that the plane of polarization rotates owing to asymmetric carbon atoms in certain organic substances when located between crossed Nicol prisms is called optical rotatory dispersion (ORD) and has been developed for molecular analysis [38]. In certain instances, and only if external magnetic forces are applied to the substance, the source radiation can pass through the optical system. The associated effects are named after the original workers involved. In the Faraday effect, the plane of polarization rotates through the substance to which the magnetic force is applied in the direction parallel to the propagation of the source radiation. Another example in which the magnetic force is applied transversely is the Cotton - Mouton effect or the Voigt effect [39]. In this instance, the source radiation can pass through the optical system because the propagating light wave is elliptically polarized through the magnetized substance. An application of the Voigt effect to the trace determination of elements has been reported [27].

The Faraday effect is related to the longitudinal Zeeman effect. As illustrated in Fig. 2, when the atomic vapour is magnetized the absorption line splits into σ^-, π and σ^+ components due to the Zeeman effect, which correspond to the transitions $\Delta M = -1$, 0 and +1, respectively, where ΔM is the difference in magnetic quantum number between the upper and lower energy levels. When the optical system is viewed in the direction of the magnetic field, the σ^- and σ^+ components are circularly polarized with clockwise and counter-clockwise motion, respectively. The π components are not observed from this position as they vibrate along the lines of magnetic force. Because plane-polarized light can be considered to be the resultant of opposite circular motions of the same frequency, the plane-polarized source radiation can be resolved into clockwise and counter-clockwise rotations. Figure 3 shows the correlation of the refractive indices of the σ^- and σ^+ components of the source radiation with the absorption coefficient, α, and the angle of rotation, ϕ. As the refractive index is inversely proportional to the propagating velocity of the motion, the clockwise motion travels slower outside and faster inside the region between the σ^- and σ^+ components. For the counter-clockwise motion, the reverse applies. Owing to the coherence, the two circular motions are synthesized to yield a plane-polarized wave. Because of the difference in velocity, the plane of the resulting light is at an angle to that of the incident light. Hence the rotatory power arises from the difference in refractive index or, in other words, it is caused by the double refraction of two circularly polarized waves through the Zeeman components σ^+ and σ^-. If there is no difference in frequency between the σ^+ and σ^- components, the refraction curves are superimposed on each other, and there is no difference between them, resulting in no rotation. This is called line-crossing. The line-crossings among hyperfine components and isotope-shifted components in the mercury line at

253.65 nm have been studied in detail [35,36].

Fig. 2. Relation between the Faraday effect and the Zeeman effect.

Fig. 3. Correlation of the angle of rotation, Φ, with the absorption coefficient, α, and the refractive index, n. $k = 2\pi\nu$, where ν is the frequency of the radiation.

1-2 Basic Theory and Expected Features

According to Malus's law, the fraction of the light energy passing through the analyzer is expressed as $\sin^2\phi$, where ϕ is the angle of rotation compared with the plane of the incident polarized light. As factors determining the transmitted intensity we must take into account the profile of the source radiation, $\rho(k)$, and the damping by atomic absorption. Thus, if the frequency is expressed in terms of angular velocity $k = 2\pi\nu$, the transmitted intensity at k, $J(k)$, can be expressed as follows:

$$J(k) = \rho(k)\,|\sin\phi(k)|^2\exp[-\alpha(k)L] \tag{1}$$

where $\alpha(k)$ is the absorption coefficient and L the length of the atomic vapour in the atomizer. In practice, we detect the integrated intensity, I:

$$I = \int_s \rho(k)\,|\sin\phi(k)|^2\exp[-\alpha(k)L]\,\mathrm{d}k \tag{2}$$

where s is the band pass of the monochromator. According to the analysis based on dispersion theory by Corney *et al.* [34] and Buckingham and Stephens [37], the rotatory power is proportional to the number of atoms in the light beam, NL, where N is the number of atoms per cubic centimeter, and the oscillator strength, f. As stated above, the rotatory power arises from the difference in refractive index, so it includes the difference between the two dispersion functions, which is called the Faraday function, $F(k,H)$. In addition, applying the Zeeman splitting to the dispersion functions, ϕ is expressed as follows:

$$\phi(k,H) \propto NLfF(k,H) \tag{3}$$

where H is the magnetic field strength.

If the number of atoms in the light beam, NL, is small enough, we can make approximations such as $\sin \phi \approx \phi$ and $\exp[-\alpha(k)L] \approx 1$. Consequently, the transmitted intensity becomes

$$I \propto (NL)^2 f^2 \int_s \rho(k) |F(k,H)|^2 \, dk \tag{4}$$

As $\rho(k)$ can be normalised as $\rho'(k) = \rho(k)/I_0$, where I_0 is the source intensity integrated over the band pass of the monochromator, $\int_s \rho(k) dk$, the transmitted intensity is expressed as follows:

$$I \propto (NL)^2 f^2 I_0 M(H) \tag{5}$$

where $M(H) = \int_s \rho'(k) |F(k,H)|^2 \, dk$.

Thus, the transmitted intensity is theoretically expected to be proportional to the square of the number of atoms in the light beam and to the source intensity, and to change as a function of the applied magnetic field strength and the line profile of the source radiation. In experimental calibration of the instrument, it is convenient to use an intensity normalized by the source intensity:

$$T = I/I_0 \text{ or } T = K(NL)^2 f^2 M(H)/\int_s \rho(k) dk \tag{6}$$

where K is a constant defined by the instrumental factors. If NL is so large that the atomic absorption is not negligible, the calibration should be made after a correction for the absorption has been applied. The corrected transmitted intensity, T_c, is given by substituting the reduced source intensity for the source intensity I_0:

$$T_c = I/\int_s \rho(k) \exp[-\alpha(k,H)L] \, dk \tag{7}$$

Use of the Faraday effect is, from the above expressions, expected to have the following advantages:

1. Those similar to atomic-fluorescence spectroscopy. As found in the above equations, the transmitted intensity increases proportionally to the source radiance, and the base-line noise is independent of the source noise.
2. Unless depolarization occurs, the light scattered by non-atomic species is blocked by the analyzer. Therefore, it has the ability to remove the positive background signal, which is a significant problem in non-dispersive atomic-fluorescence spectroscopy.
3. As the optical system is aligned, it is easy to measure the source radiation.

1-3 Early Experiment

In order to apply this principle in practical analysis, we combined the Faraday configuration with an electrothermal atomizer, and studied several fundamental characteristics of the system for cadmium, namely the dependence of the transmitted intensity on the magnetic field strength and its proportionality to the square of the number of atoms in the light beam and to the source intensity.

1-3-1 Experimental

Figure 4 illustrates the apparatus constructed for this work. It consists of a light source, polarizer, electromagnet, atomizer, analyzer, monochromator, photomultiplier tube (RCA 1P28), power supply for the atomizer, d.c. amplifier (Sanei Sokki Co.), power supply for the coils of the electromagnet, power supply for the light source, flow controller for argon gas and strip-chart recorder. A cadmium hollow-cathode lamp (Hitachi) and a cadmium electrodeless discharge lamp (EMI) were used as light sources. The former was operated in the d.c. mode and the latter mounted in a tuned cavity [40] through which microwave power of 2450 MHz was supplied. The electromagnet generated a maximum field strength of 17 kG between the pole pieces 10 mm apart with a coil current of 10 A. The pole pieces have a diameter of 20 mm and a central aperture of 3 mm diameter.

The strength of magnetic field was calibrated against the coil current by using a gauss meter (Yokokawa Co.). Glan-type prisms were employed as polarizer and analyser (Karl Lambrecht Co.). A prism monochromator was chosen for the dispersing element in order to prevent the polarization that can arise with some grating monochromators. The slit width of the monochromator was 2 mm, giving a band pass of 2.5 nm. The photocurrent due to black-body radiation from the atomizer was negligibly small.

Fig. 4. Schematic diagram of the optical system: A, microwave power supply for the electrodeless discharge lamp; B, microwave cavity; C, electrodeless discharge lamp; D, lens; E, polarizer; F, insulator; G, transformer; H, variable transformer; I, pole piece; J, graphite tube atomizer; K, graphite cone; L, solenoid coil; M, analyzer; N, gas inlet; O, power supply for the solenoid coil; P, chamber; Q, prism monochromator; R, stabilizer for high-voltage supply for the photomultiplier tube; S, d.c. amplifier; T, strip-chart recorder; and U, photomultiplier tube.

Two types of electrothermal atomizer were located in turn between the pole pieces. One was an **M**-shaped strip atomizer of tungsten, 2 mm in width [41], and the other was a graphite tube atomizer of 3 mm i.d., 5 mm o.d. and 18 mm long. The strip atomizer was attached to brass rod electrodes (4 mm in diameter), through which the atomizer was supplied with electric current. An aliquot of the sample solution was placed on the bottom of the **M**-shape. The incident beam was focused on the atomic vapour. The graphite tube atomizer was fitted to the pole pieces of the electromagnet through graphite cones, which served as thermal insulators, as shown in Fig. 5. The atomizer was supplied with electric current through the pole pieces. The sample solution was dispersed onto the bottom of the graphite tube with a syringe through a sampling port of diameter 1 mm in the middle of the lateral face of the tube. Both atomizers were enclosed in a chamber of 70 mm i.d. Argon gas was passed into the chamber and the graphite tube for purging at flow-rates of 1 ℓ min^{-1} and 50 ml min^{-1}, respectively. The latter plays an important role in reducing the contamination on the inside surface of the graphite tube by the atomic vapour. The flow of argon gas carries the atomic vapour generated by electrical heating out of the tube through the sampling port. As the temperature of the tube atomizer is highest at the port, the atomic vapour does not condense there. Thus, contamination at the edges of the tube can be prevented.

Fig. 5. Schematic diagram of the graphite tube atomizer fitted with graphite cones. All dimensions are given in millimetres.

A stock solution with a cadmium concentration of 1000 $\mu g\ ml^{-1}$ was prepared by dissolving cadmium metal in 6 N hydrochloric acid purified by distillation. Standard solutions were prepared by dilution and the acidity was adjusted to 0.1 N. Sample solution (5 μl) was removed with a microsyringe (SGE), dried at 120 °C for 1 min and atomised at an equilibrium temperature of 1000 °C for the strip atomizer and 1800 °C for the carbon tube atomizer. Because of the large capacity of the latter, its equilibrium temperature was chosen to be higher than that of the strip atomizer. A cylindrical air - acetylene flame was also examined for comparison purposes. A burner was constructed by fitting a stainless-steel tube of 6 mm i.d. to a mounting block of 30 mm o.d. The burner was connected to a conventional nebulizer for atomic-absorption spectroscopy and operated at flow-rates of 7 and 2 ℓ min^{-1} for air and acetylene, respectively. The Cd I line at 228.8 nm was chosen as the analytical line.

1-3-2 Results for cadmium and suggestion

Dependence of Transmitted Intensity on Magnetic Field Strength

Figure 6 shows the dependence of the transmitted intensity (T) on magnetic

field strength. The curve A presents the results obtained with the hollow-cathode lamp (discharge current 10 mA) and curve B those for the electrodeless discharge lamp (100 W; reflected power $\leqslant 5$ W). These curves have a maximum value at a field strength of about 3–5 kG, which we interpret as follows.

When no magnetic field is applied to the atomic vapour, the frequency of the σ^+ and σ^- Zeeman components are the same, so line-crossings occur. For this reason, the source radiation is not transmitted by the optical system. As the field strength is increased, the rotatory power is enhanced owing to the change in the relative velocity of the σ^+ and σ^- components, corresponding to the change in the term $\phi(k,H)$ in equation (2). Thus, an increasing amount of source radiation is allowed to pass through the optical system. However, too strong a field causes such a large displacement of the σ components that the source line cannot superimpose upon them. In this event, there is no region of frequency in which the source radiation is affected by the influence of the σ components, which leads to a decrease in the transmitted intensity. This corresponds to a decrease in the product $\rho(k)[\sin\phi(k,H)]^2$ in equation (3). Thus, the curve presents a miximum value, depending on the profile of the source radiation. On comparing curves A and B, it is evident that the maximum of the latter lies at a higher field strength and that its profile is broader than that of the former. Recalling the superimposition effect, the results suggest that the line profile of the radiation from the electrodeless discharge lamp is broader than that from the hollow-cathode lamp under the given conditions. This was also examined by calculating curves C and D according to equation (2). The parameters for curve C are as follows: the width of the source line was 0.2 pm, that of the absorption line 1.8 pm, the Doppler width of the absorption line 2.3 X 10^9 rad s^{-1} and the number of atoms 5 X 10^7 cm^{-2}. The parameters for curve D were the same as those for curve C, except that the width of the source radiation was larger (0.5 pm).

Fig. 6. Dependence of the transmitted intensity (T) on the magnetic field strength: A, observed curve with the hollow-cathode lamp; B, with the electrodeless discharge lamp; C and D, the calculated curves.

These calculated curves also indicate that a broader source line gives a broader curve and that the curve maximum shifts to a stronger field. Another factor that determines the curve profile is line-crossing. The effect of hyperfine structure on

line-crossings was taken into account and the Zeeman splitting pattern estimated for the analytical line at 228.8 nm. The natural abundance of cadmium is 0.875% of ^{108}Cd, 12.39% of ^{110}Cd, 12.75% of ^{111}Cd, 24.07% of ^{112}Cd, 12.26% of ^{113}Cd, 28.86% of ^{114}Cd and 9.58% of ^{116}Cd. The splitting pattern can be readily calculated for the isotopes of even relative atomic mass as they possess no nuclear spin. However, the situation is complicated for those of odd relative atomic mass because their spin momenta contribute to the Zeeman splitting. In weak fields, the nuclear spin momentum, **I**, is coupled with the electronic momentum, **J**, to yield a resultant momentum, **F**, leading to $2F + 1$ Zeeman levels in the magnetic field, where F is the total momentum quantum number. On the other hand, in a strong field, they cannot be coupled together owing to the Back - Goudsmit effect [42], but independently yield their magnetic momenta. In practice, an intermediate case exists between the two extremes.

Figure 7 shows the calculated splitting pattern for the case based on the perturbation method [43]. It is expected from Fig. 7 that a line crossing may occur at a field strength near 0.2 kG. However, contrary to expectation, no minima can be found on the curves in Fig. 6. Presumably because of Lorentz broadening of the absorption line at atmospheric pressure, the zero-field line-crossings cannot be separated from the line-crossings in question. In addition, because the natural abundance of the isotopes of odd relative atomic mass is only a quarter of the total, they have no significant effect on the shape of the curve. Another problem concerned with line-crossings is created by isotope shifts [35]. If any isotope shift exists with a displacement comparable to the broadening of the absorption line, the fall might be found on the observed curve. The results suggests that such a large shift does not occur in the cadmium line at 228.8 nm.

Calibration Graphs and Atomic Fluorescence

Figure 8 shows the relationship between the square root of the transmitted intensity and the amount of cadmium in the atomizer, *i.e.*, the calibration graphs. The lower graph (uncorrected) bends at high cadmium concentrations. The $\sqrt{T_c}$ graph is the corrected graph defined by equation (7), which includes the correc-

Fig. 7. Zeeman splitting pattern calculated for cadmium isotopes with the nuclear spin quantum numbers, $I = \frac{1}{2}$ (A) and $I = 0$ (B).

tion for atomic absorption. The atomic absorption was measured by setting the polarizer and the analyzer in a parallel configuration. The results indicate that the transmitted intensity is proportional to the square of the number of atoms. The relationship is important in measuring the phenomena observed in this work.

From the above theoretical discussion, only the rotatory dispersion induced under the magnetic field is taken into account. Atomic fluorescence of the Zeeman components might contribute to the phenomena observed. Two cases are possible. If the fluorescent radiation yields plane-polarized light synthesized in a fashion similar to that in the Faraday effect, the expression for the detected light should be

$$I = \int_s \rho(k) |\sin\phi_1 (k,H)|^2 \exp[-\alpha(k,H)L] dk + \int_s \rho(k) |\sin\phi_2 (k,H)|^2 \gamma\{1 - \exp[-\alpha(k,H)] L\} dk \quad (8)$$

where γ is the quantum yield. The first term corresponds to the Faraday effect and the second to rotation via atomic fluorescence. If the number of atoms is small enough, the second term on the right-hand side can be reduced to the expression I_2 = constant X $(NL)^3 f^3 \gamma I_0$ (under a constant field). Thus, if the fluorescence has an important role, the transmitted intensity should change as a function $C_1 (NL)^2 + C_2 (NL)^3$ under a constant field, where C_1 and C_2 are constants. The results indicate that the transmitted intensity is almost proportional to $(NL)^2$, in contrast to the above expression.

The other case, which may be the more likely, is partial depolarisation by inelastic collision between photons and atoms. For this reason, the plane-polarized radiation may become elliptically polarized and could pass through the analyzer. However, this process could also occur under zero magnetic field. The results (Fig. 6) indicate that no radiation is detected under such conditions and it therefore appears that either the fluorescent energy is negligible compared with that due to the Faraday effect, or the plane of polarization of the fluorescent radiation is the same as that of the exciting radiation and hence is blocked by the analyzer. This discussion is valid for small N, but under conditions when the number of atoms in the light beam is large the fluorescence could predominate. In the future, a detailed examination of this question will be made by checking a decay curve, using a temporal disperser of picosecond response.

Proportionality of the Transmitted Intensity to the Source Radiance

Figure 9 shows the dependence of the transmitted intensity on the intensity of the source radiation. Contrary to the prediction by equation (5), the resulting graph is not rectilinear but is concave at high source radiance, probably because the increase in lamp current causes an increase in line width. As the line width of the source radiation increases, the convolution term $\rho(k)|\sin\phi|^2$ in equation (2) becomes larger, leading to an increase in the transmitted intensity. Consequently, it could be suggested that a source radiation of higher band width is more suitable for this technique. However, theoretical calculations using equation (2) predict that too broad a line causes an increase in the rotatory power of molecular species and thus results in an unfavourable background. This was verified by introducing cigarette smoke into the graphite tube atomizer and using a D_2 lamp as the light source. Macaluso and Corbino [32] also demonstrated that magneto-optical rotation of a continuum source occurred through magnetized diatomic sodium (Na_2) as well as through the atomic vapour of sodium.

Fig. 8. Calibration graphs: $\sqrt{T}$, uncorrected for the atomic absorption and $\sqrt{T_c}$, corrected.

Fig. 9. Dependence of the transmitted intensity on the source intensity. The figures on the curve indicate the discharge lamp current in milliamperes.

Elimination of Background

Cigarette smoke was introduced into the graphite tube atomizer with the flow of argon in order to examine the ability of the system to overcome background effects. The source radiation was decreased to half of the incident power, but no background magnetic rotation signal was detected. In this technique, the depolarization of the incident radiation through the scattering process is significant for the background. However, in practice, it was found that the transmitted radiation was negligible. When 5 μl of 25 mg ml^{-1} sodium chloride solution was introduced in order to generate background, the result was the same. Thus, this technique proved to be insensitive to those background components of scattered light from which conventional atomic-absorption or atomic-fluorescence spectrometers may suffer. In this technique, there is a problem associated with a loss of incident power and transmitted energy attributable to background components, which leads to a negative interference. Nevertheless, the correction method, using T_c, enables us to overcome the interference. The operational circuits for a correction system will be described in Section 1-6-2.

Detection Limit and Reproducibility

On the basis of a signal to noise ratio of 2, the cylindrical flame atomizer gave a detection limit for cadmium of 1 μg ml^{-1}, the tungsten strip atomizer with the hollow-cathode lamp 5 X 10^{-12} g and the graphite tube atomizer with the electrodeless discharge lamp 5 X 10^{-13} g, the discharge current for the hollow-cathode lamp being 15 mA and the microwave power for the electrodeless discharge lamp 120 W. In the flame atomizer, the number of atoms in the light beam is much smaller than that in the electrothermal atomizers and therefore, owing to the dependence of the transmitted intensity on the number of atoms, *i.e.*, I = constant X $(NL)^2$, the latter atomizer is the more suitable for the present technique, as it can produce a pulse of condensed atomic cloud in the light beam. Although the tungsten strip atomizer had the advantage of less contamination, it gave less reproducible signals (the relative standard deviation was 10%) than the graphite tube atomizer (4%).

1-4 Extended Theory and Spectroscopic Features for Various Elements

In the preceding section, the author described aspects of history and principle, basic theory, predictable features, basic apparatus and experiment for cadmium. AMORS is found to be useful for the analysis of cadmium. Church *et al.* [36] and Stephens [44] applied the present method to the detection of mercury in air. Ito *et al.* [27] applied the other magneto-optical phenomenon, *i.e.*, the Voigt effect (double refraction of plane-polarized light), to the determination of cadmium. Kersey *et al.* [45], Ito *et al.* [27] and Kankare *et al.* [46] also described the basic aspects of theory of the atomic Faraday and Voigt effects.

In this section, the author wishes to develop the theoretical aspects and describe the experimental results in relation to the spectral features of various elements; the dependence of the transmitted intensity on the applied magnetic field strength, the source intensity, the line profile, and the introduced mass (calibration curve). This is intended for estimating the applicability of AMORS to the analysis of various elements. Here, novel line-crossing phenomena found in the atomic lines of various elements are described and related to the derivated theory. Such parameters as is neccessary for the practical analysis, viz. the optimum condition of the magnetic field strength and the detection limits are also given.

1-4-1 Theory correlated with Zeeman effect

The intensity of radiation transmitted through the Faraday configuration[34]is given by the following equation:

$$I(H) = \int_s \rho(k)\,|\sin\Phi(k, H)|^2 e^{-\alpha(k, H)L}\,dk. \tag{1}$$

here, $\rho(k)$ is the spectral density of the source radiation, $\Phi(k, H)$ the rotational angle of the plane of polarization, $\alpha(k, H)$ the absorption coefficient, L the length of atomic vapor, k the angular frequency, s the bandpass width of the monochromator and H the magnetic field. The rotational angle $\Phi(k, H)$ is proportional to the difference in refractive index or dispersion function between the circularly polarized light with the anti-clockwise and clockwise motions. Detail aspects of this phenomenon have been discussed in the previous papers. This is expressed by the following equations:

$$\Phi(k, H) = \left(\frac{kL\pi NP^2}{c\hbar}\right) F(k, H) = \frac{kL}{2c}(n_- - n_+), \tag{2}$$

$$F(k, H) = z\left(\frac{k - k_0 - s_1 + i\Gamma/2}{\Delta}\right) - z\left(\frac{k - k_0 - s_2 + i\Gamma/2}{\Delta}\right) \tag{3}$$

where N is the atomic density, P the matrix element for transition, c the light velocity, $\hbar = h/2\pi h$ the Planck constant, $F(k, H)$ the Faraday function, k_0 the angular frequency of the peak of the absorption line under zero field, $2\Delta\sqrt{\ln 2}$ the line width at half-maximum, Γ the reciprocal mean lifetime of the level, s_1 the Zeeman shift of the σ -component, s_2 that of σ^+-component and N the atomic density. If the number of atoms NL is small enough, we can reduce equation (1) to the following equation by making the approximation $\sin\Phi \simeq \Phi$ and $e^{-\alpha(k, H)L} \simeq 1$, we obtain the following equations:

$$I(H) \propto (NLP^2)^2 I_0 \int_s \rho'(k) F(k, H)^2\,dk, \tag{4}$$

where $I_0 = \int_s \rho(k)\,dk$ the source intensity and $\rho'(k) = \rho(k)/I_0$ the profile function of the source radiation. Consequently, the transmitted intensity is expected to be proportional to the square of the number of atoms in the light beam NL and the source intensity if the magnetic field strength and source line profile are defined.

In the practical experimental case, Lorentz broadening can be applied to the plasma dispersion function z. The Lorentzian form of the plasma dispersion function is given by the following expression:

$$z\left(\frac{k-k_0-s_1+i\Gamma/2}{\Delta}\right) = \frac{-\Delta}{k-k_0-s_1+i\Gamma/2}. \tag{5}$$

Therefore,

$$F(k, H) = \Delta\left\{\frac{k-k_0-s_2}{(k-k_0-s_2)^2+\Gamma^2/4} - \frac{k-k_0-s_1}{(k-k_0-s_1)^2+\Gamma^2/4}\right\} + i(\Delta\Gamma/2)\left\{\frac{1}{(k-k_0-s_1)^2+\Gamma^2/4} - \frac{1}{(k-k_0-s_2)^2+\Gamma^2/4}\right\}. \tag{6}$$

If the σ^- and σ^+-components have the same frequency, $s_1 = s_2$ and $F(k, H) = 0$. Therefore, the transmitted intensity is reduced to zero. As stated in the previous papers, qualitatively saying, the $\sigma^\pm$-components with the contrary circular motions cancel the rotatory power. This is called 'line-crossing'. The displacements s_1 and s_2 can be estimated by calculation of the Zeeman pattern. We shall now consider the atomic energy levels which give rise to the Zeeman pattern.

In the case of the nuclear spin $I = 0$, the change in the atomic energy is expressed by the following equation:

$$\Delta E = M_J g_J \mu_e H(\text{erg}) \quad \text{or} \quad M_J g_J L_z H(\text{cm}^{-1}) \tag{7}$$

where M_J is the magnetic quantum number $(-J, -J+1, \ldots J-1, J)$, g_J the Landé factor, μ_e the Bohr magneton, L_z the Lorentz unit and H the magnetic field strength in Gauss. The Landé factor is defined by the following expression [42]:

$$g_J = \frac{J(J+1)+S(S+1)-L(L+1)}{2J(J+1)} \tag{8}$$

where J, S and L are the quantum numbers of total angular, spin and orbital angular momenta, respectively. The displacements s_1 and s_2 are given by the selection rule:

$$\hbar s_1 = (M_{J,u} g_{J,u} - M_{J,l} g_{J,l})\mu_e H(H_z) \qquad (\Delta M_J = M_{J,l} - M_{J,u} = -1) \tag{9}$$

$$\hbar s_2 = \text{the same term as the upper } (\Delta M_J = +1), \tag{10}$$

where subscripts u and l denote the upper and lower levels, respectively.

For $I \neq 0$, there arises the hyperfine structure (hfs) with the energy change expressed by

$$\Delta E_{hfs} = \tfrac{1}{2}A'\{F(F+1) - I(I+1) - J(J+1)\} \text{ and } F = |J-I|, |J-I|+1 \ldots |J+I|-1, |J+I| \tag{11}$$

where A' is the coupling constant for coupling between J and I momenta and F the resultant momentum. In very weak fields, these hfs levels separately split into $2F+1$ sublevels with the magnetic quantum number $M_F (M_F = -F, -F+1, \ldots, F-1, F)$. The energy change in atomic level influenced by the very weak field is given by the following equation:

$$\Delta E = M_F g_F \mu_e H + \Delta E_{hfs} \tag{12}$$

where g_F is the Landé factor for *hfs*, expressed by

$$g_F = g_J \frac{F(F+1)+J(J+1)}{2F(F+1)} + g_I \frac{\mu_N}{\mu_e} \frac{F(F+1)+I(I+1)-J(J+1)}{2J(J+1)} \tag{13}$$

where μ_N is the nuclear magneton and its magnitude is *ca.* $-\mu_e/1838$; the second term is usually ignored. The selection rule for this case is $\Delta M_F = -1$, 0 and +1 and gives the transition σ^-, π and σ^+.

As the magnetic field strength increases, the coupling strength between J and I momenta decreases. In the extreme case where the coupling is completely broken down, each of J and I momenta is quantized separately. For this case, the change in atomic energy is expressed as follows;

$$\Delta E = (M_J g_J \mu_e + M_I g_I \mu_N)H + A' M_I M_J \tag{14}$$

where M_I is the magnetic quantum number of nucleus ($M_I = -I, -I+1 \ldots I-1, I$). Again, the second term in the parentheses can be omitted because of its small magnitude. The selection rule for this case is given by

$$\Delta M_J = -1(\sigma^-),\ 0(\pi) \quad \text{and} \quad +1(\sigma^+) \quad \text{with} \quad M_I = 0. \tag{15}$$

This extreme case is called the Back–Goudsmit effect.

The present problem is an intermediate situation between the above two cases, i.e. J and I momenta couple moderately. We treated the problem with the variation theorem which is frequently employed in the field of the magnetic resonance[43]. The required parturbation Hamiltonian is given by

$$\mathcal{H} = g_J \mu_e \mathbf{H} \cdot \mathbf{J} + g_I \mu_I \mathbf{H} \cdot \mathbf{I} + a \mathbf{I} \cdot \mathbf{J} + B'(\mathbf{I} \cdot \mathbf{J} - 3 I_z J_z) \tag{16}$$

where a is the constant of the Fermi interaction between J and I momenta, B' the constant of the dipole–dipole interaction between them and I_z and J_z are the projection of I and J momenta on the axis of the lines of the magnetic field, respectively. The constant A' used in equation (11) includes both of the interactions. The first and second terms represent the interactions between the magnetic field and the momenta J and I, respectively. In order to estimate the perturbation energy, the secular determinant should be defined. The diagonal elements are given by

$$\begin{aligned}
\langle JM_J IM_I | \mathcal{H} | JM_J IM_I \rangle &= g_J \mu_e \langle JM_J IM_I | \mathbf{H} \cdot \mathbf{J} | JM_J IM_I \rangle + g_I \mu_N \langle JM_J IM_I | \mathbf{H} \cdot \mathbf{I} | JM_J IM_I \rangle \\
&\quad + (a + B') \langle JM_J IM_I | \mathbf{I} \cdot \mathbf{J} | JM_J IM_I \rangle - 3B' \langle JM_J IM_I | I_z J_z | JM_J IM_I \rangle. \\
&= (g_J \mu_e M_J + g_I \mu_N M_I) H + (a + B') M_I M_J - 3B' M_I M_J \\
&= (g_J \mu_e M_J + g_I \mu_N M_I) H + (a - 2B') M_I M_J.
\end{aligned} \tag{17}$$

This corresponds to the atomic level energy for the Back–Goudsmit effect.

The non-diagonal elements which are not zero are those adjacent to the diagonal. They are given by the following equations:

$$\begin{aligned}
\langle JM_J IM_I | \mathcal{H} | JM_J - 1 IM_I + 1 \rangle &= g_J \mu_e \langle JM_J IM_I | \mathbf{H} \cdot \mathbf{J} | JM_J - 1 IM_I + 1 \rangle \\
&\quad + g_I \mu_N \langle JM_J IM_I | \mathbf{H} \cdot \mathbf{I} | JM_J - 1 IM_I + 1 \rangle + (a + B') \langle JM_J IM_I | \mathbf{I} \cdot \mathbf{J} | JM_J - 1 IM_I + 1 \rangle \\
&\quad - 3B' \langle JM_J IM_I | I_z J_z | JM_J - 1 IM_I + 1 \rangle
\end{aligned} \tag{18}$$

and

$$\langle JM_J IM_I | \mathcal{H} | JM_J + 1 IM_I - 1\rangle = g_J \mu_e \langle JM_J IM_I | \mathbf{H} \cdot \mathbf{J} | JM_J + 1 IM_I - 1\rangle$$
$$+ g_I \mu_N \langle JM_J IM_I | \mathbf{H} \cdot \mathbf{I} | JM_J + 1 IM_I - 1\rangle + (a + B')\langle JM_J IM_I | \mathbf{I} \cdot \mathbf{J} | JM_J + 1 IM_I - 1\rangle$$
$$- 3B'\langle JM_J IM_I | I_z J_z | JM_J - 1 IM_I - 1\rangle. \quad (19)$$

The first and second terms in both equations are zero because $\langle JM_J | JM_J - 1\rangle = 0$, $\langle JM_J | JM_J + 1\rangle = 0$, $\langle IM_I | IM_I + 1\rangle = 0$ and $\langle IM_I | IM_I - 1\rangle = 0$. The last terms are also zero for the same reason. The integral in the third term of equation (18) can be expressed as

$$\langle JM_J IM_I | \mathbf{I} \cdot \mathbf{J} | JM_J - 1 IM_I + 1\rangle = \langle JM_J IM_I | I_x J_x + I_y J_y + I_z J_z | JM_J - 1 IM_I + 1\rangle$$
$$= \langle JM_J | J_x | JM_J - 1\rangle\langle IM_I | I_x | IM_I + 1\rangle + \langle JM_J | J_y | JM_J - 1\rangle\langle IM_I | I_y | JM_J - 1\rangle. \quad (20)$$

Using the following equations, well-known in quantum mechanics [10]:

$$K_x | KM_K\rangle = \tfrac{1}{2}\{\sqrt{(K + M_K)(K - M_K + 1)}\, | KM_K - 1\rangle + \sqrt{(K - M_K)(K + M_K + 1)}\, | KM_K + 1\rangle\} \quad (21)$$

$$K_y | KM_K\rangle = \tfrac{i}{2}\{\sqrt{(K + M_K)(K - M_K + 1)}\, | KM_K - 1\rangle - \sqrt{(K - M_K)(K + M_K + 1)}\, | KM_K + 1\rangle\}, \quad (22)$$

we obtain the following equations:

$$J_x | JM_J - 1\rangle = \tfrac{1}{2}\{\sqrt{(J + M_J - 1)(J - M_J + 2)}\, | JM_J - 2\rangle + \sqrt{(J - M_J + 1)(J + M_J)}\, | JM_J\rangle\} \quad (23)$$

$$I_x | IM_I + 1\rangle = \tfrac{1}{2}\{\sqrt{(I + M_I + 1)(I - M_I)}\, | IM_I\rangle + \sqrt{(I - M_I - 1)(I + M_I + 2)}\, | IM_I + 2\rangle\} \quad (24)$$

$$J_y | JM_J - 1\rangle = \tfrac{i}{2}\{\sqrt{(J + M_J - 1)(J - M_J + 2)}\, | JM_J - 2\rangle - \sqrt{(J - M_J + 1)(J + M_J)}\, | JM_J\rangle\} \quad (25)$$

$$I_y | IM_I + 1\rangle = \tfrac{i}{2}\{\sqrt{(I + M_I + 1)(I - M_I)}\, | IM_I\rangle - \sqrt{(I - M_I - 1)(I + M_I + 2)}\, | IM_I + 2\rangle\} \quad (26)$$

Therefore, equation (18 and 19) are reduced to

$$\langle JM_J IM_I | \mathcal{H} | JM_J - 1 IM_I + 1\rangle = \frac{(a + B')}{2}\sqrt{(J + M_J)(J - M_J + 1)(I - M_I)(I + M_I + 1)} \quad (27)$$

and

$$\langle JM_J IM_I | \mathcal{H} | JM_J + 1 IM_I - 1\rangle = \frac{(a + B')}{2}\sqrt{(J - M_J)(J + M_J + 1)(I + M_I)(I - M_I + 1)}, \quad (28)$$

respectively. The energy values of $2F + 1$ sublevels can be estimated by subtracting ΔE from the diagonal elements and solving the secular equation. Table 1 shows the secular determinant. The blank elements are zero. The determinant is decomposed into subdeterminants of 1×1, 2×2, $3 \times 3 \ldots 3 \times 3$, 2×2 and 1×1 rows and columns.

According to the selection rule, $\Delta M_F = \Delta M_J + \Delta M_I = \pm 1(\sigma^{\pm})$ and $0(\pi)$ with $\Delta M_I = 0$, the frequency shifts of the σ^{+} and σ^{-} -components s_2 and s_1 are determined. If there arise multiple components, their shifts are defined to be $s_{2,1}, s_{2,2}, \ldots s_{2,n}$ and $s_{1,1}, s_{1,2}, \ldots s_{1,m}$. Then, equation (6) should be replaced by the following equation:

$$F(k, H) = \Delta\left\{\sum_{j=1}^{n} \frac{k - k_0 - s_{2,j}}{(k - k_0 - s_{2,j})^2 + \Gamma^2/4} - \sum_{k=1}^{m} \frac{k - k_0 - s_{1,k}}{(k - k_0 - s_{1,k})^2 + \Gamma^2/4}\right\}$$
$$+ i(\Gamma\Delta/2)\left\{\sum_{k=1}^{m} \frac{1}{(k - k_0 - s_{1,k})^2 + \Gamma^2/4} - \sum_{j=1}^{n} \frac{1}{(k - k_0 - s_{2,j})^2 + \Gamma^2/4}\right\}. \quad (29)$$

In this case, the transmitted intensity is expected to decrease partially in a given magnetic field while the region of magnetic field strength giving rise to a reduction in

the transmitted intensity is extended. In addition, line-broadening prevents the transmitted intensity from becoming zero. This will be shown for copper.

Table 1. Secular determinant for the Zeeman splitting: $\langle JM_JIM_I$ and $JM_JIM_I\rangle$ are abbreviated as $\langle M_JM_I$ and $M_JM_I\rangle$, respectively.

The Hamiltonian in Eq. (16) does not include the electric quadrupole interaction. For the case of the analytical line of gold, this seems to be significant for the Zeeman splitting pattern.

The Hamiltonian for the quadrupole interaction is given by[47]

$$H_q = B_q\left[\frac{3/2\mathbf{I}\cdot\mathbf{J}(2\mathbf{I}\cdot\mathbf{J}+1)-\mathrm{I}(\mathrm{I}-1)\mathrm{J}(\mathrm{J}+1)}{2\mathrm{I}(2\mathrm{I}-1)\mathrm{J}(2\mathrm{J}-1)}\right] \tag{30}$$

where B_q is the coupling constant for the quadrupole interaction, **I** the nuclear spin momentum, **J** the total electronic momentum, and I and J are their scalar, respectively.

The diagonal and non-diagonal elements in the secular determinant required for the perturbation calculation involve the terms $\langle \mathrm{JM_JIM_I}|\mathrm{H_q}|\mathrm{JM_JIM_I}\rangle$ and $\langle \mathrm{JM_JIM_I}|\mathrm{H_q}|\mathrm{JM_J}\mp \mathrm{kIM_I}\pm \mathrm{k}\rangle$, respectively. Here M_J and M_I are the magnetic quantum numbers of J and I, respectively and k the natural number. These elements can be expressed in terms of B_q, J, I, M_J and M_I by utilizing the common relations in quantum mechanics.

Numerical calculations were performed by a mini-computer FACOM U-200 (Fuji Tsushinki Co. Ltd.) and processed Zeeman splitting patterns were recorded out on an on-line typewriter. A portion of the processes was carried out by the computer system FACOM M-200 and data conversion system FACOM U-400 at the Nagoya University Computation Center. The programs are given in Appendix.

The coupling constants related to the hyperfine structure a and B' are estimated by a theoretical calculation with the hydrogen-like orbital and compared to values estimated by an experimental observation of the hyperfine structure by a Fabry-Perot interferometer. These values are examined also in the discussion of the line-crossing experiments. The observed hyperfine constants are cited from

the earlier work of optical experiments and recent one of novel techniques such as optical double resonance, atomic beam magnetic resonance, and level-crossing. The elements and the coupling constants are listed in Table 2, together with the other parameters. The spectral line listed are those frequently used for the analytical work in atomic absorption spectrometry.

1-4-2 Experimental

A graphite tube atomizer and air-hydrogen flame supported by toal consumption burner were used as the atomizing device. The experimental arrangement for the graphite tube atomizer is almost the same as that of the prototype used in the early work in Section 1-3, except that the source radiation is modulated by rotating the polarizer at 3600 rev. min^{-1} and that the resulting AC photocurrent is phase-rectified to remove the DC bias photocurrents caused by the blackbody radiation from the heated graphite tube atomizer (see Section 1-6). In the previous experiment of cadmium, the bias photocurrent was negligible at the wavelength of the analytical line, Cd I 228.8 nm, while it became serious at longer wavelengths of the analytical lines of the other elements, such as Cu I 324.75 nm and Ag I 328.07 nm. To permit quick recording of the curve for the dependence of the transmitted intensity on the magnetic field strength, an air-hydrogen flame supported by a total consumption burner also was used, because flames serve as a steady atom reservoir. The experimental arrangement for this purpose is shown in Fig. 1 (see also Section 1-6). An $x-y$ chart recorder (Watanabe Sokki Co. Ltd.) is used for quick recording. The abscissa servomotor of the recorder is driven by the voltage fed from the standard resister R_s located in the circuit of the coils of the electromagnet. For deep atomic absorption, the transmitted intensity in the Faraday configuration $I_\perp$ was normalized by the transmittance in the parallel or absorption configuration $I_\parallel$ (see also Section 1-3 and 1-6).

For most of elements, hollow cathode lamps (Hitachi Co. Ltd., Hamamatsu TV Co. Ltd. and Westinghouse Co. Ltd.) were used as the light sources, and operated at pulse discharge currents of 5-10 mA (mean) and 10-20 mA (peak) at 1 kHz. For cadmium and lead, electrodeless discharge lamps (EMI Co. Ltd.) also used as the light source and operated in a TE-mode cavity tuned at 2450 MHz and supplied with a microwave power of 50-120 W. Stabler and greater energy output was obtained in the longitudinal direction. In order to intensify the radiance, the bottom of the lead electrodeless discharge lamp was heated to a temperature slightly lower than a temperature at which the salt contained in the lamp moved from the bottom to the top. The top of the lamp also was heated by another heating tube so as to prevent the salt from being locally deposited. The heating tubes were wound by nichrome wire of 0.5 mm diameter and covered with quartz-alumina wool.

A Fabry-Perot interferometer (Mizojiri Kogaku Co.) was used for the determination of the *hfs* coupling constant a. This was operated by pressure scanning and had a space of 0.3045 cm between etalon plates. The radiation from the light source was dispersed by a grating monochromator (Techtron). The monochromatic radiation emerging from the exit slit was directed into the interferometer; entrance and exit slits of 0.3 mm width were employed. A pin hole of 0.5 mm diameter was utilized for separating the resulting fringes. Behind the pin hole, a photomultiplier tube (R 106 UH HTV) was located as the detector. After amplification by a d.c. amplifier (Sanei Sokki Co.), the resulting photocurrent was

displayed on an $x-y$ strip chart recorder (Watanabe Sokki Co.). The scanning pressure was converted to a voltage by a transmitter (Yokokawa Denki Co.). The voltage drove the abscissa on the $x-y$ recorder.

The flow rates of air and hydrogen were 7 $l\,min^{-1}$ and 2 $l\,min^{-1}$, respectively. The burner was mounted between the pole pieces of the electromagnet in such a way that the light beam passed through the axial centre at a height of *ca.* 15 mm above the burner top. The magnetic field strength was preliminarily calibrated against the coil current by a gaussmeter (Yokokawa Denki Co. Ltd.). Special grade reagents were used for the preparation of standard solutions throughout this experiment. The concentration of all solutions except of the Sn solution (10,000 $\mu g\,ml^{-1}$) was adjusted to 1,000 $\mu g\,ml^{-1}$ of analyte.

For the other elements such as vanadium, barium, aluminum and platinum, no optical energy could be detected. This is probably due to the low degree of atomization in the air-hydrogen flame.

The purge gas, argon was introduced into the graphite tube atomizer and the enclosing chamber at flow rates of 50 ml min^{-1} and 1.5 $l\,min^{-1}$, respectively. Five μl of sample solution was dispensed into the graphite tube atomizer by means of a micropipette (Muromachi Kagaku), dried at 120°C for a minute and atomized at temperatures of 1400-1800°C. The atomization temperature was measured by an optical pyrometer (Tokyo Hokushin Denki). The magnetic field strength was calibrated by a gaussmeter (Yokokawa Denki). Special grade reagents were used for preparation of standard solutions throughout this experiment.

Fig. 1. Schematic diagram of the experimental arrangement: a = hollow cathode lamp; b = polarizing prism; c = lens; d = electromagnet; e = air-hydrogen flame; f = analyzing prism, g = aperture; h = prism monochromator; i = plane mirror; j = photomultiplier tube (R955); k = photomultiplier tube (R306); l = a.c. amplifier; m = bandpass filter and phase-sensitive amplifier; n = off-set amplifier; o = operational amplifier for dividing and square root processing; p = $X-Y$ recorder; q = pulse generator; r = current-stabilizing power supply; s = voltage-stabilizing power supply and t = rectifier.

Table 2. Analytical lines observed and associated parameters

Isotopes	I [58]	Abundance % [58]	Wavelength nm [59]	Transition [60]	Hyperfine constants 10^{-3} cm^{-1}
^{6}Li	1	7.4	670.784	$2s^2S_{1/2}-2p^2P^{\circ}_{3/2}$	
			670.789	$2s^2S_{1/2}-2p^2P^{\circ}_{1/2}$	
^{7}Li	3/2	92.6	670.784	$2s^2S_{1/2}-2p^2P^{\circ}_{3/2}$	$A(^2S_{1/2})=13.40$ [11], $B'(^2P^{\circ}_{3/2})=-0.102$ [49]
				$2s^2S_{1/2}-2p^2P^{\circ}_{1/2}$	$B'(^2P^{\circ}_{1/2})=1.54$ [11], $B_q(^2P^{\circ}_{3/2})=-0.006$ [49]

^{23}Na	3/2	100	588.995	$3s^2S_{1/2}-3p^2P^\circ_{3/2}$	$A(^2S_{1/2})=29.5[11]$, $B'(^2P^\circ_{3/2})=0.622$ **[49]**
			589.592	$3s^2S_{1/2}-3p^2P^\circ_{1/2}$	$B'(^2P^\circ_{1/2})=3.15[11]$, $B_q(^2P^\circ_{3/2})=0.094$ **[49]**
^{39}K	3/2	93.1	766.495	$4s^2S_{1/2}-4p^2P^\circ_{3/2}$	$A(^2S_{1/2})=7.7[11]$, $B'(^2P^\circ_{3/2})=0.203$ **[49]**
			769.898	$4s^2S_{1/2}-4p^2P^\circ_{1/2}$	$B'(^2P^\circ_{1/2})=3.15[11]$, $B_q(^2P^\circ_{3/2})=0.0924$ **[49]**
^{41}K	3/2	6.3	766.495	$4s^2S_{1/2}-4p^2P^\circ_{3/2}$	
			769.898	$4s^2S_{1/2}-4p^2P^\circ_{1/2}$	
^{85}Rb	5/2	72.15	780.023	$5s^2S_{1/2}-5p^2P^\circ_{3/2}$	$A(^2S_{1/2})=33.75[11]$, $B'(^2P^\circ_{3/2})=0.835$ **[49]**
			794.760	$5s^2S_{1/2}-5p^2P^\circ_{1/2}$	$B'(^2P^\circ_{1/2})=4.026[11]$, $B_q(^2P^\circ_{3/2})=0.868$ **[49]**
^{87}Rb	3/2	27.85	780.023	$5s^2S_{1/2}-5p^2P^\circ_{3/2}$	$A(^2S_{1/2})=113.98[11]$, $B'(^2P^\circ_{3/2})=2.83$ **[49]**
			794.760	$5s^2S_{1/2}-5p^2P^\circ_{1/2}$	$B'(^2P^\circ_{1/2})=13.56[11]$, $B_q(^2P^\circ_{3/2})=0.417$ **[49]**
^{133}Cs	7/2	100	852.110	$6s^2S_{1/2}-6p^2P^\circ_{3/2}$	$A(^2S_{1/2})=76.66[11]$, $B'(^2P^\circ_{3/2})=1.68$ **[49]**
					$B_q(^2P^\circ_{3/2})=0.417[11]$
^{25}Mg	5/2	10.13	285.121	$3s^{21}S_0-3s3p^1P^\circ_1$	$B'(^1P^\circ_1)=0.51[15]$, $0<B_q(^1P^\circ_1)<0.53$ **[50]**
$^{24,26}Mg$	0	89.87	285.212	$3s^{21}S_0-3s3p^1P^\circ_1$	
^{43}Ca	7/2	0.145	422.673	$4s^{21}S_0-4s4p^1P^\circ_1$	$B'(^1P^\circ_1)=-0.26[15]$, $\lvert B_q(^1P^\circ_1)\rvert<0.40$ **[50]**
$^{40,42,44,46,48}Ca$	0	99.86	422.673	$4s^{21}S_0-4s4p^1P^\circ_1$	
^{87}Sr	9/2	2.02	460.735	$5s^{21}S_0-5s5p^1P^\circ_1$	$B'(^1P^\circ_1)=-0.11[15]$, $B_q(^1P^\circ_1)=1.3$ **[50]**
$^{84,86,88}Sr$	0	97.98	460.735	$5s^{21}S_0-5s5p^1P^\circ_1$	
^{67}Zn	5/2	4.11	213.856	$4s^{21}S_0-4s4p^1P^\circ_1$	$B'(^1P^\circ_1)=0.592[12]$
$^{64,66,68,70}Zn$	0	95.89	213.856	$4s^{21}S_0-4s4p^1P^\circ_1$	
^{197}Au	3/2	100	242.795	$6s^2S_{1/2}-6p^2P^\circ_{3/2}$	$A(^2P^\circ_{3/2})=107[13]$, $B'(^2P^\circ_{3/2})=0.467$ **[51]**
					$B_q(^2P^\circ_{3/2})=10.93[14]$
^{53}Cr	3/2	9.55	357.869	$3d^54s^7S_3-3d^44s4p^7P^\circ_4$	
$^{50,52,54}Cr$	0	90.45	357.869	$3d^54s^7S_3-3d^44s4p^7P^\circ_4$	
^{55}Mn	5/2	100	279.482	$3d^54s^{26}S_{5/2}-3d^54s4p^6P^\circ_{7/2}$	$B'(^6S_{5/2})=0[16]$, $B'(^6P^\circ_{7/2})=16.0$ **[52]**
			279.827	$^6P^\circ_{5/2}$	$B'(^6P^\circ_{5/2})=18.5[17]$
			280.106	$^6P^\circ_{3/2}$	$B'(^6P^\circ_{3/2})=23.0[17]$
			403.076	$3d^54s^{26}S_{5/2}-3d^54s4p^6P^\circ_{7/2}$	$B'(^6P^\circ_{7/2})=-13.4[17]$
			403.307	$^6P^\circ_{5/2}$	$B'(^6P^\circ_{5/2})=-18.3[17]$
			403.449	$^6P^\circ_{3/2}$	$B'(^6P^\circ_{3/2})=-22.1[17]$

Table 2. cont'd

Isotopes	I [58]	Abundance % [58]	Wavelength nm [59]	Transition [60]	Hyperfine constants 10^{-3} cm^{-1}
^{57}Fe	1/2	2.19	248.327	$3d^64s^25D_4-3d^64s4p^5F^\circ_5$	$B'(^5D_4)=1.270$ [53]
$^{54,56,58}Fe$	0	97.81	248.327	$3d^64s^25D_4-3d^64s4p^5F^\circ_5$	
^{59}Co	7/2	100	240.725	$3d^74s^24F_{9/2}-3d^74s4p^4G^\circ_{11/2}$	$B'(^4F_{9/2})=15.02$ [54,55] $B_q(^4F_{9/2})=4.644(19)$, 4.658 [55]
^{61}Ni	3/2	1.19	232.003	$3d^84s^23F_4-3d^84s4p^3G^\circ_5$	$B'(^3F_4)=-7.173(21)$, $B_q=-1.897$ [56]
$^{58,60,62,64}Ni$	0	98.81	232.003	$3d^84s^23F_4-3d^84s4p^3G^\circ_5$	
^{115}Sn	1/2	0.35	286.333	$5s^25p^23P_0-5s^25p6s^3P^\circ_1$	
^{117}Sn	1/2	7.61	286.333	$5s^25p^23P_0-5s^25p6s^3P^\circ_1$	$A(^3P^\circ_1)=-159.57$ [57]
^{119}Sn	1/2	8.58	286.333	$5s^25p^23P_0-5s^25p6s^3P^\circ_1$	$A(^3P^\circ_1)=-167.01$ [57]
$^{112,114,116,118,120,122,124}Sn$	0	83.46	286.333	$5s^25p^23P_0-5s^25p6s^3P^\circ_1$	

Isotope	I	Term	Fermi constant a (c^{-1}) calc.	obs.	B-O constant B' (c^{-1}) calc.	obs.
^{63}Cu ^{65}Cu	3/2 3/2	$5p^2P_{3/2}$	0	–	-1.6×10^{-6} ($m_J=\pm1/2$) 1.6×10^{-6} ($m_J=\pm3/2$)	–
		$4p^2P_{1/2}$	0	–	0	–
		$4s^2S_{1/2}$	0.0713	0.195, 0.195*	0	–
^{107}Ag ^{109}Ag	1/2 1/2	$5p^2P_{3/2}$	0	–	2.1×10^{-7} ($m_J=\pm1/2$) -2.1×10^{-7} ($m_J=\pm3/2$)	–
		$5s^2S_{1/2}$	0.0068	–	0	–
^{111}Cd ^{113}Cd	1/2	$5s5p^1P_1$	0	–	-3.2×10^{-4} ($m_l=0$) 1.6×10^{-4} ($m_l=\pm1$)	-0.0447
		$5s^2\,{}^1S_0$	0	–	0	–

1-4-3 Dependence of the transmitted intensity on the magnetic field strength

The dependence of the transmitted intensity on the magnetic field is the primarily important parameter of AMORS for determining the optimum condi-

tion for analytical work.

Copper. A resonance line Cu I 324.75 nm was chosen as the analytical line. Figure 2 shows the dependence of the transmitted intensity on the magnetic field strength. In the zero field, the $\sigma^{\pm}$-components superimpose each other. This is so-called zero field line crossing, in which no energy can pass through the Faraday configuration. As the magnetic field becomes stronger, they are separated. This causes the increasing rotatory power, and the source radiation is allowed to pass through the optical system. However, too strong field causes such a large displacement of the σ-components that the source line can not superimpose upon them. This reduces the region of frequency in which the source radiation interacts with the σ-components. For this reason, the transmitted intensity decreases as the magnetic field increases beyond the strength about 8 kG. This corresponds to a decrease in the product $\rho(k)\,|\sin\Phi(k, H)|^2$ in equation (1).

We note that there is a sharp minimum on the curve. This is expected to be assignable to the line-crossing. The natural abundance of copper is 69.1% of ^{63}Cu and 30.9% of ^{65}Cu. Both isotopes have a nuclear spin momentum of $I = 3/2$. In the zero field, the coupling $\mathbf{F} = \mathbf{I} + \mathbf{j}$ gives rise to *hfs* with $F|I-j| \ldots |I+j|$. For the upper level of the analytical line $^2P_{3/2}$, sublevels $^2_3P_{3/2}$, $^2_2P_{3/2}$, $^2_1P_{3/2}$ and $^2_0P_{3/2}$ arise. In very weak fields, each of the *hfs* sublevels splits into $2F+1$ magnetic sublevels with $M_F = -F, 1-F, \ldots, F-1, F$. For the upper level, $7+5+3+1$ magnetic sublevels are totally produced. The lower level $^2S_{1/2}$ changes into $^2_2S_{1/2}$ and $^2_1S_{1/2}$ which give $5+3=8$ magnetic sublevels. In weak fields (so-called compared with the strong field to which the Paschen–Back effect applies.), the coupling between $\mathbf{I}$ and $\mathbf{j}$ is perfectly released

Fig. 2. Dependence of the transmitted intensity on the magnetic field strength for Cu I 324.75 nm.

(the Back–Goudsmit effect), as referred to in the preceding theory. In this case, the level energy is determined by the combination of M_I and m_j. However, the total number of the resulting magnetic sublevels does not alter, keeping the relation $M_F = M_I + m_j$. In Table 3, they are listed for the two extreme cases. The *hfs* coupling constants a and B' are listed in Table 2. Figures 3 and 4 show the theoretical Breit–Rabi levels of the upper and lower levels. Since B' for the upper level is very small, the pattern is almost identical to that for the case of no coupling or $I = 0$. Figure 5 illustrates the transition between them. This predicts that the line-crossings between the σ-components occur in a region of magnetic field of 0.8–1.4 kG. On the other

hand. the experimental result indicates that line-crossings arise in a region of the magnetic field of 3–4.5 kG. This discrepancy is probably either due to an erroneous value of the coupling constant a or due to an error in estimating the effective nuclear charge Z on the electron or in employing the hydrogenlike orbital. Figures 6–8 show the Zeeman patterns calculated by varying the value of the coupling constant a.

Figure 9 shows the *hfs* obtained by the Fabry–Perot intereferometer for the analytical line Cu I 324.75 nm. The experimental value of the coupling constant a estimated from the interferogram is listed in Table 1 together with those reported by the other investigators [48].

Figure 9 shows the *hfs* obtained by the Fabry–Perot interferometer for the analytical line Cu I 324.75 nm. The experimental value of the coupling constant a estimated The transition indicates that the line-crossings occur in a region of the magnetic field of 2–4.2 kG. Thus, if an experimentally determined a-value is employed for calculations of the variation theorem, the dependence of the transmitted intensity can be predicted with a good agreement with the experimental result, even for the case in which there arise *hfs* and the intermediate coupling between **I** and **J** momenta. From this result, it is

Table 3. Two extreme cases of the Zeeman splitting for Cu I 324.75 nm

No field	Very weak field (hfs Zeeman effect)		Weak field (Back-Goudsmit effect)			
Term	M_F	g_F	M_I	M_J	g_J	
$^2_3P_{3/2}$	3	2/3	3/2	3/2	4/3	upper state
	2		3/2	1/2		
	1		3/2	-1/2		
	0		3/2	-3/2		
	-1		1/2	3/2		
	-2		1/2	1/2		
	-3		1/2	-1/2		
$^2_2P_{3/2}$	2	2/3	1/2	-3/2		
	1		-1/2	3/2		
	0		-1/2	1/2		
	-1		-1/2	-1/2		
	-2		-1/2	-3/2		
$^2_1P_{3/2}$	1	2/3	-3/2	3/2		
	0		-3/2	1/2		
	-1		-3/2	-1/2		
$^2_0P_{3/2}$	0	2/3	-3/2	-3/2		
$^2_2S_{1/2}$	2	1/2	3/2	1/2	2	lower state
	1		3/2	-1/2		
	0		1/2	3/2		
	-1		1/2	-1/2		
	-2		-1/2	1/2		
$^2_1S_{1/2}$	1	-1/2	-1/2	-1/2		
	0		-3/2	1/2		
	-1		-3/2	-1/2		

Fig. 3. Change in energy ΔE for the upper level of copper $4p^2P_{3/2}$ vs the magnetic field strength H, calculated using the calculated a- and B'-values.

Fig. 4. ΔE vs H for the lower level of copper $4s^2S_{1/2}$, calculated using the calculated a- and B'-values.

Fig. 5. Zeeman splitting pattern for CuI 324.75 nm: (+) σ^+-component, (.) σ^--component and (*) the line crossing between them. The assignments of the lines of the Zeeman pattern in this figure and subsequent figures are summarized in the Appendix.

Figs. 6–8. Variation in the Zeeman splitting pattern with the a-value for the lower level.

Fig. 7.

Fig. 8.

Fig. 9. Trace of scanned interferogram for Cu I 324.75 nm.

Fig. 11. ΔE vs H for the lower level of copper $^2S_{1/2}$, calculated with the experimental a-value.

Fig. 12. Zeeman splitting pattern for Cu I 324.75 nm, calculated with the experimental a-value for the lower level: (‖) π-component.

marked that the effective nuclear charge for the s-electron of copper might be larger ($Z=4.2$) than that expected ($Z=3.1$) owing to its penetrating character. The B'-constant cannot be experimentally obtained because of its small value and the broadening of the absorption lines. However, if the experiment of the atomic Faraday spectroscopy be carried out with an atomizer evacuated, the constant may be determined. It is likely that the effective nuclear charge for the non-penetrating p-electron is different from that for the penetrating s-electron. The behaviour of the sublevel for the lower state is very interesting in that the region in which deep coupling between **I** and **j** occurs is only up to a field of about 0.8 kG and that the almost extreme situation of the Back–Goudsmit effect arises near a field of 10 kG.

The results of other studies of the line-crossing [61], in which the ratio of the atomic absorption of $\sigma^{\pm}$ to π-components was measured, agree with our prediction and experimental results.

Figure 13 shows the dependence of the transmitted intensity on the magnetic field strength for the other resonance line 327.40 nm which arises from the same electron configuration of the upper state but a different term ($4s^2S_{1/2}-4p^2P_{1/2}$). It is obvious that no line-crossings take place. Figures 14 and 15 demonstrate the calculated Breit–Rabi levels and transition. It is theoretically predicted that no line-crossing occurs for this line regardless of the magnitude of the a-constant. From an analytical point of view, this line may be preferable to the line 324.7 nm for the sharp dip due to the line-crossings interferes with the stability of the transmitted intensity if any variation in magnetic flux exists.

Fig. 13. Dependence of the transmitted intensity on the magnetic field strength for Cu I 327.40 nm.

Fig. 14. ΔE vs. H for the upper level of copper $4p^2P_{1/2}$, calculated with the calculated a- and B'-values.

Fig. 15. Zeeman splitting pattern for Cu I 327.40 nm, calculated with the experimental a-value for the lower level.

Silver. Figure 16 shows the dependence of the transmitted intensity on the magnetic field strength, for the analytical line of Ag I 328.07 nm ($5s^2S_{1/2}-5p^2P_{3/2}$). It is apparent from Fig. 16 that no significant line-crossing takes place. The natural abundance of silver is 51.85% of ^{107}Ag and ^{109}Ag. Both isotopes have a nuclear spin momentum of $I=1/2$. The calculated a and B'-constants are listed in Table 3. The examination by the Fabry–Perot interferometer indicated that the line was single. This was also found in an other experiment [62]. As expected from the calculated coupling constant, the Fermi-contact effect is in practice small for the 5s-electron. Figures 17–19 show the calculated levels for the upper and lower levels, and the transition, respectively. Here, the upper level changes into *hfs* $^2_2P_{3/2}$ and $^2_1P_{3/2}$ while the lower level changes into $^2_1S_{1/2}$ and $^2_0S_{1/2}$. The former splits into $5+3=8$ magnetic sublevels and the latter into $3+1=4$ magnetic sublevels. The calculated transition pattern predicts that

Fig. 16. Dependence of the transmitted intensity on the magnetic field strength for Ag I 328.07 nm.

no line-crossings take place for this line irrespective of the magnitude of the a-constant. The reduction in the transmitted intensity with an increase in magnetic field beyond about 7 kG is interpreted in the same manner as for the copper line. Because of the different nuclear spin momentum, there arises no line-crossing for the line of silver resulting from the transition between the same terms as those of copper. Of the same group of elements, gold isotope ^{197}Au(100% natural abundance) has a nuclear spin momentum of $I = 3/2$, and the calculated a-value for the $6s$-electron has a magnitude comparable to that for the $4s$-electron of copper. Therefore, some line-crossings are expected for the analytical line Au I 242.80 nm ($^2S_{1/2} - {}^2P_{3/2}$). The results for gold will be described.

Cadmium. The analytical line of cadmium Cd 228.8 nm is the result of the transition $5s^2\ {}^1S_0$–$5s5p\ {}^1P_1$. The natural abundance of cadmium is 0.857% of ^{108}Cd, 12.39% of ^{110}Cd, 12.75% of ^{111}Cd, 24.07% of ^{112}Cd, 12.26% of ^{113}Cd, 28.86% of ^{114}Cd and 9.58% of ^{116}Cd. The isotopes with even atomic mass have a nuclear spin momentum $I = 0$ while those with odd mass a momentum $I = 1/2$. For the former case, there arises no hfs. Under a magnetic field, the upper level splits into magnetic sublevels with $M_J = -1$, 0 and 1, and the lower levels are unchanged. For the latter isotopes, *hfs* ${}_{3/2}^{1}P_1$ and ${}_{1/2}^{1}P_1$ arise from the upper level and ${}_{1/2}^{1}S_0$ from the lower. The former *hfs* split into $4+2=6$ magnetic sublevels and the latter into two magnetic sublevels. For the isotopes with $I = 0$, the Zeeman splitting pattern can be readily caculated by equation (7), while to those with $I = 1/2$ the variation theorem should be applied.

The function of Dirac electron for two valence electrons has not been given. However, in the lower state, the relative anti-parallel spins produce no apparent Fermi interaction, i.e. $a = 0$. For the upper state, the Fermi interaction by $5s$-electron should be corrected by the following expression [42]:

$$a' = a(g_J - 1)/2.$$

As $g_J = 1$ for ${}^1P_1$ term, $a' = 0$. Since the resultant spin momentum $S = 0$, the remaining momentum is the angular momentum $=1$. Because no L–S coupling is formed in this case, the dipole–dipole coupling constant B' is calculated by substituting the Schrödinger wave function of the $5p$-electron for the Dirac electron. An experimental value of B' for ${}^1P_1$ has been estimated by the other investigators [63]. We also attemped to determine the value by the scanning of the Fabry–Perot interferometer. Although self-reversal was revealed, no pronounced result informing us of the interaction was manifested. The calculated and earlier reported values are listed in Table 3. Figures 20–22 demonstrate the Breit–Rabi levels for the upper and lower states, and the transition calculated with the experimental value of B', respectively. Although the calculated pattern predicts a line-crossing at a field strength of about 0.2 kG, between a σ^--component for $I = 0$ and a σ^+-component for $I = 1/2$, the experimental result, shown in Fig. 23, does not distinctly indicate it. Probably, the effect is concealed by the Lorentz broadening of the components. In addition, because of the natural abundance of the isotopes with odd atomic mass is only a quarter of the total, they have no significant effect on the shape of the curve.

Alkali elements

The analytical lines of alkali elements are assigned to the transition $n\mathrm{s}^2\mathrm{S}_{1/2} - n\mathrm{p}^2\mathrm{P}_{1/2}$, ${}^2\mathrm{P}_{3/2}$ where n is the principal quantum number.

Sodium

The natural abundance of sodium is 100% of ^{23}Na with the nuclear spin momentum $I = 3/2$. There arise hyperfine levels ${}^2_1\mathrm{S}_{1/2}$ and ${}^2_2\mathrm{S}_{1/2}$ from the lower level ${}^2\mathrm{S}_{1/2}$, ${}^2_1\mathrm{P}_{1/2}$ and

$^2_2P_{1/2}$ from the upper level $^2P_{1/2}$, and $^2_0P_{3/2}$, $^2_1P_{3/2}$, $^2_2P_{3/2}$ and $^2_3P_{3/2}$ from the upper level $^2P_{3/2}$. Each hyperfine level splits into $2F+1$ sublevels in a magnetic field. Because the magnitude of the coupling constants for the dipole–dipole and quadrupole interactions is small, the effect of the hyperfine structure in the upper levels on the splitting pattern is expected to be negligible for both D-lines. Figure 24 and 25 demonstrate the calculated Zeeman splitting patterns for the D_1 and D_2-lines, respectively. It is expected that independently of the magnitude of the coupling constant A no line-crossings occur between the σ^+ and σ^--components in the D_1-line. On the other hand, in the D_2-line, line-crossings are expected to occur in a region of magnetic field strength near 0.4 kG. Figures 26 and 27 show the experimentally found dependence of the normalized transmitted intensity or transmittance in the Faraday configuration ($I_\perp/I_\parallel$) on the magnetic field strength (H) for the D_1 and D_2-line, respectively and Fig. 28 shows the dependence of $I_\parallel$ on H for the D_2-line, where $I_\perp$ is the source radiation transmitted through such an optical system that the polarizer and analyzer are in the crossed configuration or the Faraday configuration and $I_\parallel$ that transmitted through the system in the parallel configuration or the atomic absorption configuration.

As expected above, no dips associated with line-crossings are found on the curve $I_\perp/I_\parallel$ vs H for the D_1-line. Contrarily to the prediction, however, no dips are recognizable on the curve for the D_2-line either. As stated previously, this may be attributable to the small magnitude of the separation among the hyperfine components. Owing to Lorentz/Doppler broadening in the $\sigma^\pm$-components, the crossing region spreads out and is not discriminated from the region of the zero-field line-crossings.

The curve $I_\parallel$ vs H shows a simple increase in the transmittance or a simple decrease in atomic absorption. This reflects an outward movement of the $\sigma^\pm$-components from the region of the source line profile as the magnetic field increases.

Fig. 17. ΔE vs. H for the upper level of silver $5p^2P_{3/2}$, calculated with the calculated a- and B'-values.

Fig. 18. ΔE vs. H for the lower level of silver $5s^2S_{1/2}$, calculated with the calculated a- and B'-values: the a-value has been corrected by multiplying with the ratio of the experimental to calculated values for copper.

Fig. 19. Zeeman splitting pattern for Ag I 328.07 nm, calculated with the calculated a- and B'-values.

Fig. 20. ΔE vs H for the upper level of cadmium $5s5p\,^1P_1$, calculated with the experimental B'-value: curves are plotted for both isotopes ($I = 0$ and 1/2).

Fig. 21. ΔE vs. H for the lower level of cadmium $5s^2\,^1S_0$.

Fig. 22. Zeeman splitting for Cd I 228.80 nm, calculated with the experimental B'-value for the upper level.

Fig. 23. Dependence of the transmitted intensity on the magnetic field strength for Cd I 228.80 nm.

Fig. 24. Calculated Zeeman splitting pattern of the line Na I 589.592 nm (+) = σ -component, (·) = π -component, H = magnetic field strength, S = frequency displacement.

Fig. 25. Calculated Zeeman splitting pattern of the line Na I 588.995 nm; (*) line-crossing between the σ^+ and σ^--components.

Fig. 26. Dependence of the transmitted intensity on the magnetic field strength for the line Na I 589.592 nm; $I_\perp$ = transmitted intensity in the crossed configuration, $I_\parallel$ = transmitted intensity in the parallel configuration.

Fig. 27. $I_{\perp}/I_{\parallel}$ vs H for Na I 588.995 nm.

Fig. 28. Dependence of the transmittance in the parallel configuration on the magnetic field strength; $I_{\parallel}$. o = source intensity.

Potassium

The natural abundance of potassium is 93.1% of ^{39}K and 6.9% of ^{41}K, both of which have a nuclear spin momentum I = 3/2. Figures 29 and 30 demonstrate the dependence of $I_{\perp}/I_{\parallel}$ on H for the D_1 and D_2-lines. No dips are found on the curves, which is attributable to the same causes as those for the case of the sodium D-lines. The calculated Zeeman splitting pattern indicates that line-crossings in the D_2-line occur at magnetic field strengths lower than 0.2 kG. Although the coupling constants have not been known for the isotope ^{41}K, its influence on the curves might be minor because of its small abundance.

Lithium

The natural abundance of lithium is 7.4% of ^{6}Li with I = 1 and 92.6% of ^{7}Li with I = 3/2. Figure 31 shows the curve $I_{\perp}/I_{\parallel}$ vs H. This result involves those for both D-lines because of very small separation between the D-lines. In contrast to sodium and potassium, lithium has an isotope with I = 1 (^{6}Li). However, the presence of the isotope may not affect the curve profile since its abundance is very small and the coupling constants are smaller in magnitude than those for the participant levels of isotope ^{7}Li. Therefore, the curve profile is expected to be defined mostly by the degree

Fig. 29. $I_\perp/I_\parallel$ vs H for K I 769.898 nm

Fig. 30. $I_\perp/I_\parallel$ vs H for K I 766.491 nm.

Fig. 31. $I_\perp/I_\parallel$ vs H for Li I 670.784 nm.

of hyperfine interaction in isotope ^{7}Li. The calculated Zeeman splitting patterns indicate that no line-crossings take place in the D_1-line while line-crossings occur near 0.2 kG. Contrarily to this, however, no dips associated with line-crossings are found on the curve. This is attributable to the same causes as those for the case of sodium or potassium.

In contrast to the curve for sodium or potassium, the curve for lithium does not

have a maximum at fields up to 8.5 kG. This might be partly attributable to the following. In this case, the molar concentration was so high that atomic absorption was strong (89.5%) at zero-field and still so at 8.5 kG (80.0%). In such a situation, the line profile of the $\sigma^{\pm}$-components is distorted due to Holtsmark broadening. This greatly favours the superposition of the absorption lines over the source line. Line broadening is known to be significant for lines of light atoms. For these reasons, the frequency region of the interaction between the source radiation and absorption line (the $\sigma^{\pm}$-components) is extended, resulting in the displacement of the curve maximum towards stronger fields. As described previously, this is partly responsible for the curvature of the calibration curve at high concentration of atoms.

Rubidium

The natural abundance of rubidium is 72.15% of ^{85}Rb with I = 5/2 and 27.85% of ^{87}Rb with I = 3/2. The coupling constants of the lower level for both isotopes are much larger in magnitude than those for sodium, potassium and lithium. Therefore, it is expected that line-crossings will occur in the D_2-line. The calculations of the Zeeman splitting pattern indicate that no line-crossings occur in the D_1-line for both isotopes. Figure 32 demonstrates the dependence of $I_{\perp}/I_{\parallel}$ on H for the D_1-line. Consistently

Fig. 32. $I_{\perp}/I_{\parallel}$ vs H for Rb I 794.760 nm.

with expectation, no dips related to line-crossings are appreciable on the curve. Figures 33 and 34 show the calculated Zeeman splitting patterns of the D_2-line for the isotopes ^{85}Rb and ^{87}Rb, respectively. Line-crossings are expected to occur at magnetic fields between 0.4 and 1.2 kG for isotope ^{85}Rb and between 1.0 and 2.4 kG for isotope ^{87}Rb. Figure 35 shows the dependence of $I_{\perp}/I_{\parallel}$ on H. Inconsistently with prediction, no dips attributable to line-crossings are found on the curve. This might be elucidated as follows. The rotatory power is decreased also by line-crossings between the $\sigma^{\pm}$-components in the absorption lines for the different isotopes as well as for the same isotopes. In this case, the region of line-crossings is not determined by the simple summation of the region of line-crossings for ^{85}Rb and ^{87}Rb but extended by line-crossings between the σ^{+}-components of ^{85}Rb and the σ^{-}-components of ^{87}Rb, and between the σ^{+}-components of ^{87}Rb and the σ^{-}-components of ^{85}Rb. Thus, the overall region of line-crossings extends almost continuously from the zero-field line-crossings to 2.4 kG. Furthermore, the effect of line-crossings on the experimental curve profile should be significant near the zero-field because of the larger abundance of ^{85}Rb. Owing to line broadening of the components, line-crossings are not discriminated from zero-field line-crossings, resulting in an indistinct dip on the curve.

Cesium

The natural abundance of cesium is 100% of ^{133}Cs with I = 7/2. Figure 36 demonstrates the calculated Zeeman splitting pattern of the D_2-line. Line-crossings are expected to take place at magnetic fields near 1.8 kG. Figures 37 and 38 show the experimental curves of $I_\perp/I_\parallel$ and $I_\parallel$ vs H, respectively. In agreement with the prediction, a dip attributable to line-crossings is found on the former curve. A small maximum is found on the atomic absorption curve. A similar phenomenon was shown for the analytical line of copper Cu I 324.754 nm in the study of Zeeman AAS by Oishi *et al.*[64]. This may be also interpreted as follows. The σ^--components separated from the hyperfine component at higher frequency (A_H in Fig. 36) and the σ^+-components from that at lower frequency (A_L in Fig. 36) move out of the frequency regions of the corresponding hyperfine components of the source line (in Fig. 36 S_H and S_L, respectively), as the magnetic field strength increases. This causes a decrease in atomic absorption. Subsequently, A_H and A_L shift into S_L and S_H, respectively, leading to a recovery of the atomic absorption. As the magnetic field strength further increases, A_H and A_L disappear from the frequency of regions of the source line, resulting again in a decrease in atomic absorption.

Fig. 33. S vs H for Rb I 780.023 induced in the isotope ^{85}Rb with the nuclear spin momentum I = 5/2.

Fig. 34. S vs H for Rb I 780.023 induced in the isotope ^{87}Rb with I = 3/2.

Fig. 35. $I_\perp/I_\parallel$ vs H for Rb I 780.023 nm.

Fig. 36. S vs H for Cs I 852.110 nm; $A_H = \sigma^-$-components displaced from the hyperfine component at the higher frequency of the absorption line, $A_L = \sigma^-$-components displaced from the hyperfine component at the lower frequency, S_H = hyperfine component at the higher frequency of the source radiation, S_L = hyperfine component at the lower frequency.

Fig. 37. $I_\perp/I_\parallel$ vs H for Cs I 852.110 nm.

Fig. 38. $I_\parallel/I_{\parallel,0}$ vs H for Cs I 852.110 nm.

Alkaline earth elements

The analytical lines of alkaline earth elements are assigned to the transition $ns^2{}^1S_0$-$nsnp\,{}^1P_1$. The natural abundance of isotopes of alkaline earth elements, possessing a nuclear spin momentum is 10.1% of ^{25}Mg (I = 5/2), 0.15% of ^{43}Ca (7/2) and 2.02% of ^{87}Sr (I = 9/2). Since the isotopes without spin momentum preponderate, the effect of hyperfine structure is expected to be not notably reflected on the curve of $I_\perp/I_\parallel$ vs H, even if the participant electron and nucleus are strongly coupled. Figures 39-41 show the curves of $I_\perp/I_\parallel$ vs H for the analytical lines of the alkaline earth elements. As expected, no dips associated with line-crossings are found on the curves. Figure 42 demonstrates the calculated Zeeman splitting pattern for the transition ${}^1S_0 - {}^1P_1$ (I = 0).

Zinc

Because of the same type of transition as those for the analytical line of alkaline earth elements, the small abundance of the isotope with a nuclear spin momentum (4.1% of ^{67}Zn with I = 5/2) and the small magnitude of the coupling constant of the upper level for ^{67}Zn, line-crossings do not affect the experimental curve of $I_\perp/I_\parallel$ vs H. Figure 43 shows the curve. As expected, no dips are found on the curve. The curve maximum is not found up to 8 kG. This is attributable to the same reason as that for the case of the lithium line.

Fig. 39. $I_\perp/I_\parallel$ vs H for MgI 285.213 nm.

Fig. 40. $I_\perp/I_\parallel$ vs H for Ca I 422.673 nm.

Fig. 41. $I_\perp/I_\parallel$ vs H for Sr I 460.733 nm.

Fig. 42. S vs H for the transition $^1S_0$–$^1P_1$ induced in the isotope of alkaline earth elements with I = 0.

Fig. 43. $I_{\perp}/I_{\parallel}$ vs H for Zn I 213.856 nm.

Gold

Figure 44 and 45 show the experimentally obtained curves of $I_{\perp}$ vs H for the analytical lines Au I 242.795 and 267.595 nm, respectively. There is no dips due to line-crossings for the latter line while a dip for the former line. Because of the same types of transition as those for the two analytical lines of copper, the difference can be easily elucidated from the difference in Zeeman splitting pattern. However, the dip for the gold line is relatively wide and shallow, compared with that for the line CuI 324.754 nm. Preliminary calculation of the Zeeman splitting pattern indicates that if the experimental value of A is used, the magetic field strength at which the minimum of the dip lies is correctly predicted. However, broadening of the dip cannot yet be explained. It must be partly attributable to the relatively large magnitude in the quadrupole interaction ($B_q = 0.01093$ cm^{-1} [51]). Figure 46 shows the calculated Zeeman splitting pattern for Au I 242.795 nm, which involves quadrupole interaction. Compared to the previously calculated pattern, the region of line-crossings is extended due to broadening in regions occupied by the $\sigma^{\pm}$-components. In addition to this, there may be some contribution to the shallow dip resulting from the fact that, because of line-crossings at lower field than that for the case of the copper line, the extent of superimposing over the zero-field line crossings is higher. In other words, this case is an intermediate one between those for the copper and rubidium lines.

Fig. 44. Dependence of the transmitted intensity on the magnetic field strength for the line of Au I 242.795 nm

Fig. 45. Dependence of the transmitted intensity on the magnetic field strength for the line of 267.595 nm

Fig. 46. S vs H for Au I 242.795 nm.

Transition metals

Chromium. The natural abundance of chromium is 9.6% of ^{53}Cr (I = 3/2), 4.3% of ^{50}Cr, 83.8% of ^{53}Cr and 2.4% of ^{54}Cr. Since the isotopes except ^{53}Cr in small abundance have no nuclear spin momentum, the hyperfine structure may not be reflected on the curve of $I_{\perp}/I_{\parallel}$ vs H. Figure 47 shows this curve. Because of the wide bandpass of the monocromator, the neighbouring lines, Cr I 359.349 and 360.535 nm partly participate in the result. As expected, no dips are found on the curve. Line-crossings are caused also by the isotope shift. In this case, however, the result indicates the absence of such a large isotope shift that it exceeds line-broadening. Figure 48 shows the calculated Zeeman splitting pattern of Cr I 357.869 nm for the isotope with I = 0.

Manganese. The natural abundance of manganese is 100% of ^{55}Mn with I = 5/2. Figures 49 and 50 show the curve of $I_{\perp}/I_{\parallel}$ vs H for a set of the triplet lines of manganese, Mn I 279.482, 279.287 and 280.106 nm, and that for the other set, Mn I 403.076, 403.307 and 403.449 nm, respectively. No dips related to line-crossings are recognized on the curves. Since the coupling constant B′ is relatively large for all the lines, line-crossings are expected to be present. This inconsistency can be explained as follows. Figure 51 shows the calculated Zeeman splitting pattern for Mn I 403.075 nm. The patterns for the other lines are similar to this pattern, except there is a slight difference in the displacement rate of the $\sigma^{\pm}$-components and the region of line-crossings. The figure indicates line-crossings continuously take place from zero-field to 5 kG. For the same reason as that referred to in the case of rubidium, the dip due to line-crossings can not be distinguished from that at zero-field.

Iron. The natural abundance of the iron isotopes with a nuclear spin momentum is 2.2% of ^{57}Fe (I = 1/2) alone. Therefore, for the same reasons as for the case of the

analytical line of chromium, the contribution of its hyperfine structure to the curve is expected to be small. Figure 52 shows the curve of $I_\perp$ vs H for the analytical line of iron. Because of the wide bandpass of the monochromator, the lines Fe I 246.264, 248.673 and 250.113 nm are partly associated with the curve. As expected, no dips are found on the curve. Figure 53 shows the calculated Zeeman splitting pattern of the line Fe I 248.372 nm for the isotopes with I = 0. A similar result was obtained for the other analytical line Fe I 252.285 nm.

Cobalt. The natural abundance of cobalt is 100% of ^{59}Co with I = 7/2. Figure 54 demonstrates the curve of $I_\perp$ vs H for the analytical line Co I 40.725 nm. For same reason as for the iron lines, the other resonance lines Co I 238.486 and 242.493 nm may partly affect the curve profile. Any reasonably determined values of B′ for the upper level have not been proposed, so that the complete Zeeman splitting

Fig. 47. $I_\perp/I_\parallel$ vs H for Cr I 357.869 nm.

Fig. 48. S vs H for Cr I 357.869 nm induced in the isotopes of chromium with I = 0.

Fig. 49. $I_\perp/I_\parallel$ vs H for Mn I 272.482, 279.287 and 280.106 nm.

Fig. 50. $I_\perp$ vs H for Mn I 403.076, 403.307 and 403.449 nm.

Fig. 51. S vs H for Mn 403.076 nm.

Fig. 52. $I_{\perp}$ vs H for Fe I 248.327 nm.

Fig. 53. S vs H for Fe I 248.327 nm induced in the isotopes of iron with I = 0.

Fig. 54. $I_\perp$ vs H for Co I 240.725 nm.

pattern for Co I 240.725 nm cannot be estimated. However, taking into account the hyperfine structure in the other line, Co I 252.236 nm [65], the mode of line-crossings might be similar to that of the manganese lines. For this reason, no dips related to line-crossings are found on the curve.

Nickel. The natural abundance of nickel is 67.8% of ^{58}Ni, 26.2% of ^{60}Ni, 3.7% of ^{62}Ni, 1.2% of ^{64}Ni with I = 0 and 1.2% of ^{61}Ni with I = 3/2. Because of the minor abundance of ^{61}Ni, no dips associated with line-crossings are expected to be present on the curve $I_\perp/I_\parallel$ vs H (Fig. 55). Figure 56 demonstrates the calculated Zeeman splitting pattern of Ni I 232.003 nm for the isotopes with I = 0.

Tin. The natural abundance of the tin isotopes with nuclear spin momentum is 0.35% of ^{115}Sn, 7.6% of ^{117}Sn and 8.6 % of ^{119}Sn with I = 1/2. Their total amount is only 16.5% and consequently their contribution to the curve $I_\perp/I_\parallel$ may be minor (Fig. 57). In agreement with the expectation, no dips are found on the curve. Figure 58 demonstrates the calculated Zeeman splitting pattern of Sn I 286.333 nm for the isotopes with I = 0. The isotope shift is known for the other line [66]. If the shift is

Fig. 55. $I_\perp/I_\parallel$ vs H for Ni I 232.003 nm.

Fig. 56. S vs H for Ni I 232.003 nm induced in the isotopes of nickel with I = 0.

Fig. 57. $I_{\perp}/I_{\parallel}$ vs Sn I 286.333 nm.

Fig. 58. S vs H for Sn I 286.333 nm induced in the isotopes of tin with I = 0.

present in Sn I 286.333 nm, line-crossings are expected. However, this is not reflected on the curve. Owing to line broadening, the dips due to this might be incorporated into zero-field line-crossings.

Lead

The natural abundance of lead is 1.4% of ^{204}Pb, 25% of ^{206}Pb, 22% of ^{207}Pb and 52% of ^{208}Pb. Only isotope ^{207}Pb has a nuclear spin momentum $I = 1/2$, whereas $I = 0$ for the others. The analysis line Pb I 283.31 nm is assigned to the transition between the terms $6s^26p^2(1/2, 1/2)_0$ and $6s^26p7s(1/2, 1/2)_1$ which result from the j–j coupling scheme. For isotope ^{207}Pb, the nuclear momentum couples with the total inner momentum of the electrons **J** to yield a resultant momentum **F**. Consequently, there arise hyperfine terms ${}_{1/2}(1/2, 1/2)_0{-}_{1/2}(1/2, 1/2)_1$, ${}_{3/2}(1/2, 1/2)_1$ where the left-hand subscripts indicate the resultant momentum F. Thus, it is expected that two hyperfine components arise in the analysis line emitted from isotope ^{207}Pb.

In addition to the hyperfine structure, the isotope shift effect is notable for the analysis line of lead. According to the zero-field line structure observed by KOPFERMAN [67], the complete Zeeman splitting pattern was estimated. Figure 59 demonstrates the calculated pattern where the contribution of isotope ^{204}Pb is ignored because of its small abundance.

Figure 60 shows the experimental result of the dependence of the transmitted intensity on the magnetic field strength. The curve feature is accounted in the same

fashion as discussed in previous section. In zero field, the σ-components (σ^+ and σ^-) are not separated from each other, which is the so-called "zero-field line crossing." Then, no rotatory power arises and the source radiation cannot pass through the optical system. As the magnetic field strength increases, the σ-components are separated from each other and the rotatory power is enhanced to result in an increase in the transmitted flux. Because of the limited width of the source line profile, a too strong field displaces the σ-components far from the frequency region of the source line profile. In this situation, the σ-components cannot interact with the source radiation. For this reason, the transmitted flux decreases at fields stronger than about 6 kG.

Fig. 59. Zeeman splitting pattern calculated for the analytical line Pb I 283.31 nm. (a) lines for the isotope ^{206}Pb, (b) ^{207}Pb and (c) ^{208}Pb.

Fig. 60. Dependence of the transmitted intensity, $I_\perp$ on the magnetic field strength, H for the analysis line. The light source is a hollow cathode lamp operated at a discharge current of 15 mA and the introduced mass of lead is 5×10^{-9} g.

Another factor causing curvature is the line-crossing between the σ^+ and σ^- components other than the zero-field line crossing. At the field strength where such line crossing occurs, the transmitted intensity should decrease. From Fig. 59, it can be predicted that the line crossings take place at field strengths lower than 2 kG. From Fig. 60, however, it is found that no significant dips are noticed around there. This is presumably attributable to the following. Because of line broadening of the σ^- components, crossing near 0.6 kG is incorporated with zero-field line crossings. Since crossing is ascribed to the isotope with even mass nucleus, the total abundance of which

amounts to 77%, this predominantly contributes to the curve profile. The other crossings at stronger field strengths can be distinguished from zero-field line crossings. However, their contribution is minor since the abundance of the participant isotope ^{207}Pb is only 22%. For physical purposes a detailed identification of line crossings could be made by evacuating the atomizer so as to reduce Lorentz broadening.

Antimony

The natural abundance of antimony is 57.25% of ^{121}Sb and 42.75% of ^{123}Sb. The former isotope has a nuclear spin momentum of $I = 5/2$ and the latter $I = 7/2$. The analytical line Sb I 231.147 nm is assigned to the transition $5s^25p^3\ ^4S_{3/2} - 5s^25p^26s\ ^4P_{1/2}$. The total electronic momentum **J** couples with the nuclear spin momentum **I** to yield a resultant momentum **F**, the magnitude of which is $F = |I-J|, |I-J+1|, \ldots, |I+J-1|$ and $|I+J|$. In very weak fields, there arise $2F+1$ magnetic sublevels with the respective magnetic quantum numbers $M_F = -F, -F+1, \ldots, F-1$ and F. In stronger fields (called weak fields when compared to those causing the Paschen–Back effect), the coupling between **I** and **J** is broken, which is called the Back–Goudsmit effect [68]. In this situation, the energy level is determined by the set of M_I and M_J. In practice, there arises an intermediate situation between the above two extremes. The number of the resulting magnetic sublevels does not change and is equal to $2F+1$. For the isotope ^{121}Sb, the lower energy term $^4S_{3/2}$ consists of hyperfine levels $^4_1S_{3/2}$, $^4_2S_{3/2}$, $^4_3S_{3/2}$ and $^4_4S_{3/2}$. In magnetic field, these split into 3, 5, 7 and 9 magnetic sublevels, respectively. The upper term $^4P_{1/2}$ consists of hyperfine levels $^4_2P_{1/2}$ and $^4_3P_{1/2}$ which split into 5 and 7 magnetic field, these split into 3, 5, 7 and 9 magnetic sublevels, respectively. The hyperfine levels $^4_2S_{3/2}$, $^4_3S_{3/2}$, $^4_4S_{3/2}$ and $^4_5S_{3/2}$. When magnetic fields are applied to atoms, these levels are separated into 5, 7, 9 and 11 magnetic sublevels, respectively. For the calculation of the Zeeman splitting pattern by the variation theorem, the coupling constant A for the penetrating electron (the Fermi contact effect) and B' for the non-penetrating electron (the dipole–dipole interaction) should be known or estimated. An equation applicable to the complex electron configuration has been reported earlier [42]. This involves several quantum numbers and g_I-factor. The experimental approach to estimate the coupling constants was also made by scanning the hyperfine structure by means of a Fabry–Perot interferometer.

Figure 61 shows the dependence of the transmitted intensity on the magnetic field strength for Sb I 231.147 nm. In the zero field, the $\sigma^{\pm}$-components overlap each other. This is so-called zero field line crossing. At this point, there does not arise any rotatory power and no optical energy can pass through the Faraday configuration. As the magnetic field strength increases, the components are separated from each other and the source radiation is allowed to pass through. However, too strong fields cause so large a displacement of the $\sigma^{\pm}$-components that they can not interact with the source radiation. For this reason, the transmitted intensity decreases at higher fields, which give rise to a maximum on the curve.

The curve does not show a minimum or dip which would represent line crossing in addition to the zero field line crossing. Figure 62 shows the Zeeman splitting pattern theoretically calculated with the calculated hyperfine constants for Sb 231.147 nm. There are theoretically predictable line crossing points in a very weak field region of up to 0.4 kG. However, the experimental result does not indicate such crossing points. This can be related to such a small magnitude of the coupling constant that the separation among the hyperfine components is concealed by Doppler/Lorentz broadening. As a result, line crossings appear to be incorporated into zero-field line crossings. To confirm the hyperfine structure in the zero field, the line Sb I 231.147 nm was

analysed by the Fabry–Perot interferometer. Under a condition of a d.c. discharge current of 10 mA, no definitive discrimination among the hyperfine components was observed, though slightly recognizable shoulders were observable on both slopes of the line profile. If the atomization chamber were evacuated to reduce the Lorentz broadening in the absorption line, the curve of the transmitted intensity vs the magnetic field strength would reflect line crossings clearly.

Fig. 61. Dependence of the transmitted intensity of the line Sb I 231.15 nm on the magnetic field strength: pulse rate = 300 s^{-1}, pulse current = 200 mA, introduced mass of Sb = 100 ng.

Fig. 62. Zeeman splitting pattern of Sb I 231.15 nm, calculated with the calculated hyperfine coupling constants: (+) = σ^+-component, (.) = σ^--component, (*) = line-crossing between the σ^+ and σ^--components. Plottings for the isotopes with I = 7/2 and 5/2 are superimposed at fields of up to 5.2 kG and parts of the line assignment are listed in the Appendix, of this section.

The analytical line Bi I 306.772 nm is assigned to the transition $6s^26p^3\,{}^4S_{3/2}-6s^26p^27s\,{}^4P_{1/2}$. The natural abundance of bismuth is 100% of ^{209}Bi with a nuclear spin momentum I = 9/2. From the lower level ${}^4S_{3/2}$ arise the hyperfine levels ${}^4_3S_{3/2}$, ${}^4_4S_{3/2}$, ${}^4_5S_{3/2}$ and ${}^4_6S_{3/2}$ due to coupling between **J** and **I** momenta. In magnetic fields, these are separated into 7, 9, 11 and 13 magnetic sublevels, respectively. The upper level ${}^4P_{1/2}$ involves ${}^4_4P_{1/2}$ and ${}^4_5P_{1/2}$, which give 9 and 11 magnetic sublevels, respectively. The other analytical line Bi I 223.061, often employed in atomic absorption spectrometry, is assigned to the transition $6s^26p^3\,{}^4S_{3/2}-6s^26p^26d\,{}^2D_{5/2}$. This is the inhibited transition because $\Delta L = 2$. In spite of this, its transition probability is rather large. From the upper term ${}^2D_{5/2}$ arise the hyperfine levels ${}^2_2D_{5/2}$, ${}^2_3D_{5/2}$, ${}^2_4D_{5/2}$, ${}^2_5D_{5/2}$, ${}^2_6D_{5/2}$ and ${}^2_7D_{5/2}$, which split into 5, 7, 9, 11, 13 and 15 magnetic sublevels in magnetic fields, respectively.

Figure 63 demonstrates the dependence of the transmitted intensity on the magnetic field strength for the line Bi I 306.772 nm. It is noteworthy that a deep and broad dip is found on the curve. This is expected to be a result of many line crossings between the σ^+ and σ^--components. This result does not agree with the calculated pattern if the calculated value is used for the coupling constant A. The experimental value was determined from the interferogram [68] and used for the calculation. Figure 64 shows the interferogram of Bi I 306.772 nm. From this, the coupling constant A for 7s electron in the upper level is determined to have a value of 0.191 cm^{-1}. The constant B'

Fig. 63. Dependence of the transmitted intensity of the line Bi I 306.77 nm on the magnetic field strength: pulse rate = 1000 s^{-1}, peak current = 200 mA, introduced mass of Bi = 5 ng.

Fig. 64. Typical interferogram of the line Bi I 306.77 nm: lamp current = d.c. 10 mA. Line broadening was found for the lamp operated in the pulse mode.

Fig. 65. Energy splitting pattern of the lower level $6s^26p^3\,^4S_{3/2}$, calculated with a tentatively adopted B'-constant of zero.

for the dipole–dipole interaction seems to have a small value. Accordingly, the value could not be determined from the interferogram and the calculation was performed with the assumption of zero value. Figures 65-67 show the calculated patterns of the upper and lower levels and the transition, respectively. This indicates that line crossings between σ^+ and σ^--components exist in a region between 2.6 and 5.8 kG. Although the experimental and theoretical results roughly agree with each other as to the magnetic field strength at which the lines begin to cross, there is a discrepancy in that line crossings considerably extend beyond the predicted magnetic strength of 5.8 kG. This might be related to an erroneous estimation of the B'-value. Calculations with tentative values of the constant B indicate that the upper limit of the crossing region is displaced towards stronger or weaker fields and the crossing region is extended or narrowed for B'-values of negative and positive sign respectively. Therefore, it is suggested that the constant B' has a negative sign for the lower level.

Figure 68 illustrates the dependence of the transmitted intensity on the magnetic field strength for the other analytical line Bi I 223.061 nm. There is a small dip on the curve. This also is expected to be attributable to line crossings. However, the theoretical calculation of the splitting pattern of this line is very complicated because of large values of J and I momenta. The result will be described elsewhere. Figure 69 shows the interferogram of the line Bi I 223.061 nm. It can be noted that a weak satellite line lies beside the stronger line. Probably, line crossings between σ^+ and σ^--components resulting from these lines cause the small dip on the curve. Since the participant electrons are 6p and 6d electrons, the hyperfine structure should be attributed mainly to the dipole–dipole interaction between the electrons and nuclei. As shown in the

interferogram of the line Bi I 306.772 nm, the interaction by the 6p electron does not significantly affect the hyperfine structure. Since 6p electron in the lower level is common for both of the analytical lines, the hyperfine structure in the line Bi I 223.061 nm could be attributed chiefly to the effect of the 6d electron.

Fig. 66. Energy splitting pattern of the upper level $6s^26p^27s\ ^4P_{1/2}$, calculated with the A-constant experimentally determined by the interferometric measurement.

Fig. 67. Zeeman splitting pattern of the line Bi I 306.77 nm, calculated from the energy splitting patterns: line assignments are listed in the Appendix, of this section.

Fig. 68. Dependence of the transmitted intensity of the line Bi I 223.06 nm on the magnetic field strength: pulse rate = 1000 s^{-1}, peak current = 200 mA, introduced mass of Bi = 40 ng.

Fig. 69. Typical interferogram of the line Bi I 223.06 nm: pulse rate = 1000 s^{-1} and peak current = 200 mA.

1-4-4 Dependence of the transmitted intensity on the source radiance

The dependence of the transmitted intensity on the source radiance is also one of the important parameters. Figures 70-72 show the relations for the analytical lines of copper, cadmium and lead. Contrarily to expectation by equation (4), the experimental graphs are not rectilinear but somewhat concave at high source radiance. Presumably, the increase in lamp current causes an increase in line width of the source radiation. As the line width increases, the convolution term $\rho'(k)\,|\sin\Phi(k, H)|^2$ in equation (6) becomes larger, leading to an increase in the transmitted intensity. The dependence of the transmitted intensity on the line width of the source radiation was calculated by numerical integration. Since the pressure in the light source is low, the Gaussian form is applied to the source profile function $\rho'(k)$. Figure 73 shows the result of the calculation. The calculation coincides with the experimental results. For practical purposes, it is pointed out that a radiation source with a greater line width is preferable for the present technique than that with a narrow one. This originates from the displacement of the σ-components from the original frequency. In atomic absorption spectrometry, the line-broadening of source radiation is a disadvantage as the sensitivity in absorption is reduced, while in the present technique it is an advantage. Alternatively, a tunable light source could be used preferably. A magnetized electrodeless discharge lamp or a tunable laser could be utilized as such light source.

Fig. 70. Dependence of the transmitted intensity on the source radiance for Cu I 324.75 nm.

Fig. 71. Dependence of the transmitted intensity on the source radiance for Cd I 228.80 nm.

Fig. 72. Dependence of the transmitted intensity, $I_{\perp}$ on the radiance of the light source, I_0. Numbers indicate the microwave power supplied to the electrodeless discharge lamp in watts. The introduced mass of lead is 2.5×10^{-10} g.

Fig. 73. Theoretical curve of the dependence of the transmitted intensity on the line-width of source radiation.

1-4-5 Calibration curve of square law dependence and detection limit

The calibration curve and detection limit also are the important factors for the analytical purpose. It is predicted by the theoretical expressions and shown in Sec. 1-3 that the intensity of light transmitted through the Faraday configuration is proportional to the square of the number of atoms in the light beam. The calibration curve of square law dependence is quite unique, compared with those for the other methods. Figure 74 shows the calibration lines for some elements. As predicted theoretically, the transmitted intensity is proportional to the square of the introduced mass of element. The dynamic range extends beyond 10^2. This is comparable to that by atomic absorption spectrometry. Beyond the linear region, however, the curve bends or becomes a function in lower power than square. Though the detail is not clear, the following causes are possible. The approximation used in the derivation of the expressions, *i.e.*, $\sin\Phi \simeq \Phi$ where Φ is the rotational angle and $\Phi \propto NL$ (see Sec. 1-3 and 1-4-1), does not hold for large values of N. However, this might not be the major cause because the absolute transmittance in the Faraday configuration is up to 10^{-3} to 10^{-2} for the

calibration regions. Another cause is a distortion in the absorption line with the increase in the density of atomic vapor, which is encountered in atomic absorption spectromentry. Since the interaction between the source radiation and σ-components occurs in the wing-to-wing fashion, it could reflect the distortion in the profile of the absorption line. A promising technique for overcoming the problem is to make the frequency regions of the source radiation and σ-components coincide. For this purpose, it may be effective to use as the light source such a wide line-profile source as a high pressure discharge lamp, or such wavelength-shifted sources as a tunable dye laser and a Zeeman shifted lamp located in a magnetic field.

Fig. 74 Calibration line

● : Manganese, ◆ : Gold, ○ : Cobalt, □ : Nickel

Detection limits for various elements, which were practically measured on the basis of S/N ratio = 2, are listed in Table 3, together with the other optimum conditions. The optimum temperatures of the graphite tube atomizer are almost the same as those for atomic absorption spectrometry with electrothermal atomization. It should be emphasized in the analytical sense that the lowest working region for quantitative analysis lies closely to the detection limit because the spectral intensity becomes strong drastically as a function of square of the introduced mass, as shown in Fig. 75. Therefore, the concentration working region usable for the practical analysis by AMORS is closer to the detection limit, compared with those by AAS ($I/I_0 \propto \exp(-\propto N)$) and AES($I \propto N$).

Fig. 75 Square-law dependence

Table 3 Detection limit

Element	Line (nm)	H (kG)	Atom. Temp. (°C)	D.L. (10^{-12}g)
Cd	228.8	5.0	1600	0.5+
Ag	328.1	6.0	1800	2*
Cu	324.7	2.5	1800	3*
Sb	231.1	5.0	2000	500*
Bi	306.8	3.5	2000	50*
Au	242.8	3.5	1750	50
Co	240.7	3.5	2050	20
Ni	232.0	2.8	2050	17
Pb	283.3	6.0	1800	50+
Mn	403.1	3.0	1900	2
Cr	357.8	1.2	2100	500

Lamp current is 10 mA (mean)

+Electrodeless discharge lamp

*High pulse mode: 200 mA (peak)

Appendix

Assignments of the lines of the Zeeman splitting patterns.

The assignment of each line is given in terms of M_J and M_I for the lower and upper level, respectively. The 'column number' designating the line is counted in each figure from bottom to top at 10 kG.

Table A1.

Figure	Column	Lower level M_J	Lower level M_I	Upper level M_J	Upper level M_I
5	71	0.5	1.5	1.5	1.5
	9	0.5	1.5	−0.5	1.5
	92	−0.5	1.5	0.5	1.5
	30	−0.5	1.5	−1.5	1.5
	73	0.5	0.5	1.5	0.5
	11	0.5	0.5	−0.5	0.5
	90	−0.5	0.5	0.5	0.5
	28	−0.5	0.5	−1.5	0.5
	75	0.5	−0.5	1.5	−0.5
	12	0.5	−0.5	−0.5	−0.5
	89	−0.5	−0.5	0.5	−0.5
	26	−0.5	−0.5	−1.5	−0.5
	76	0.5	−1.5	1.5	−1.5
	14	0.5	−1.5	−0.5	−1.5
	87	−0.5	−1.5	0.5	−1.5
	24	−0.5	−1.5	−1.5	−1.5
6	74	0.5	0.0	1.5	0.0
	11	0.5	0.0	−0.5	0.0
	90	−0.5	0.0	0.5	0.0
	27	−0.5	0.0	−1.5	0.0
7	70	0.5	1.5	1.5	1.5
	8	0.5	1.5	−0.5	1.5
	93	−0.5	1.5	0.5	1.5
	31	−0.5	1.5	−1.5	1.5

Table A1. (Cont'd)

Figure	Column	Lower level M_J	Lower level M_I	Upper level M_J	Upper level M_I
	72	0.5	0.5	1.5	0.5
	10	0.5	0.5	−0.5	0.5
	91	−0.5	0.5	0.5	0.5
	29	−0.5	0.5	−1.5	0.5
	75	0.5	−0.5	1.5	−0.5
	12	0.5	−0.5	−0.5	−0.5
	88	−0.5	−0.5	0.5	−0.5
	26	−0.5	−0.5	−1.5	−0.5
	77	0.5	−1.5	1.5	−1.5
	15	0.5	−1.5	−0.5	−1.5
	86	−0.5	−1.5	0.5	−1.5
	23	−0.5	−1.5	−1.5	−1.5
8	63	0.5	1.5	1.5	1.5
	1	0.5	1.5	−0.5	1.5
	41	−0.5	1.5	−1.5	1.5
	68	0.5	0.5	1.5	0.5
	5	0.5	0.5	−0.5	0.5
	97	−0.5	0.5	0.5	0.5
	35	−0.5	0.5	−1.5	0.5
	73	0.5	−1.5	1.5	−0.5
	11	0.5	−0.5	−0.5	−0.5
	90	−0.5	−0.5	0.5	−0.5
	28	−0.5	−0.5	−1.5	−0.5
	80	0.5	−1.5	1.5	−1.5
	18	0.5	−1.5	−0.5	−1.5
	78	−0.5	−1.5	0.5	−1.5
	16	−0.5	−1.5	−1.5	−1.5
12	67	0.5	1.5	1.5	1.5
	35	0.5	1.5	0.5	1.5
	5	0.5	1.5	−0.5	1.5
	98	−0.5	1.5	0.5	1.5
	67	−0.5	1.5	−0.5	1.5
	36	−0.5	1.5	−1.5	1.5
	70	0.5	0.5	1.5	0.5
	39	0.5	0.5	0.5	0.5
	8	0.5	0.5	−0.5	0.5
	94	−0.5	0.5	0.5	0.5
	63	−0.5	0.5	−0.5	0.5
	31	−0.5	0.5	−1.5	0.5
	74	0.5	−0.5	1.5	−0.5
	43	0.5	−0.5	0.5	−0.5
	12	0.5	−0.5	−0.5	−0.5
	89	−0.5	−0.5	0.5	−0.5
	58	−0.5	−0.5	−0.5	−0.5
	26	−0.5	−0.5	−1.5	−0.5
	79	0.5	−1.5	1.5	−1.5
	48	0.5	−1.5	0.5	−1.5
	17	0.5	−1.5	−0.5	−1.5
	82	−0.5	−1.5	0.5	−1.5
	51	−0.5	−1.5	−0.5	−1.5
	20	−0.5	−1.5	−1.5	−1.5
15	27	0.5	1.5	0.5	1.5
	12	0.5	1.5	−0.5	1.5
	91	−0.5	1.5	0.5	1.5
	75	−0.5	1.5	−0.5	1.5
	31	0.5	0.5	0.5	0.5
	15	0.5	0.5	−0.5	0.5

Table A1. (Cont'd)

Figure	Column	Lower level M_J	Lower level M_I	Upper level M_J	Upper level M_I
	87	−0.5	0.5	0.5	0.5
	71	−0.5	0.5	−0.5	0.5
	35	0.5	−0.5	0.5	−0.5
	19	0.5	−0.5	−0.5	−0.5
	82	−0.5	−0.5	0.5	−0.5
	66	−0.5	−0.5	−0.5	−0.5
	40	0.5	−1.5	0.5	−1.5
	24	0.5	−1.5	−0.5	−1.5
	75	−0.5	−1.5	0.5	−1.5
	59	−0.5	−1.5	−0.5	−1.5
19	75	0.5	0.5	1.5	0.5
	42	0.5	0.5	0.5	0.5
	11	0.5	0.5	−0.5	0.5
	90	−0.5	0.5	0.5	0.5
	59	−0.5	0.5	−0.5	0.5
	26	−0.5	0.5	−1.5	0.5
	74	0.5	−0.5	1.5	−0.5
	42	0.5	−0.5	0.5	−0.5
	11	0.5	−0.5	−0.5	−0.5
	90	−0.5	−0.5	0.5	−0.5
	59	−0.5	−0.5	−0.5	−0.5
	27	−0.5	−0.5	−1.5	−0.5
22	77	0.0	0.5	1.0	0.5
	50	0.0	0.5	0.0	0.5
	24	0.0	0.5	−1.0	0.5
	72	0.0	−0.5	1.0	−0.5
	51	0.0	−0.5	0.0	−0.5
	29	0.0	−0.5	−1.0	−0.5
	74	0.0	0.0	1.0	0.0
	51	0.0	0.0	0.0	0.0
	27	0.0	0.0	−1.0	0.0

Table A2

Figure	Column	Lower level M_J	Lower level M_I	Upper level M_J	Upper level M_I
62	12	1.5	1.5	0.5	1.5
	88	−1.5	3.5	−0.5	3.5
	12	1.5	0.5	0.5	0.5
	89	−1.5	2.5	−0.5	2.5
	11	1.5	−0.5	0.5	−0.5
	89	−1.5	1.5	−0.5	1.5
	10	1.5	−1.5	0.5	−1.5
	89	−1.5	0.5	−0.5	0.5
	10	1.5	−2.5	0.5	−2.5
	90	−1.5	−0.5	−0.5	−0.5
	9	1.5	−3.5	0.5	−3.5
	91	−1.5	−1.5	−0.5	−1.5
	91	−1.5	−2.5	−0.5	−2.5
	92	−1.5	−3.5	−0.5	−3.5
67	41	1.5	4.5	0.5	4.5
	11	0.5	4.5	−0.5	4.5
	40	1.5	3.5	0.5	3.5
	89	−0.5	4.5	0.5	4.5
	12	0.5	3.5	−0.5	3.5
	38	1.5	2.5	0.5	2.5
	59	−1.5	4.5	−0.5	4.5
	88	−0.5	3.5	0.5	3.5
	14	0.5	2.5	−0.5	2.5
	37	1.5	1.5	0.5	1.5
	60	−1.5	3.5	−0.5	3.5
	86	−0.5	2.5	0.5	2.5
	16	0.5	1.5	−0.5	1.5
	35	1.5	0.5	0.5	0.5
	62	−1.5	2.5	−0.5	2.5
	85	−0.5	1.5	0.5	1.5
	17	0.5	0.5	−0.5	0.5
	33	1.5	−0.5	0.5	−0.5
	63	−1.5	1.5	−0.5	1.5
	83	−0.5	0.5	0.5	0.5
	20	0.5	−0.5	−0.5	−0.5
	31	1.5	−1.5	0.5	−1.5
	65	−1.5	0.5	−0.5	0.5
	81	−0.5	−0.5	0.5	−0.5
	22	0.5	−1.5	−0.5	−1.5
	29	1.5	−2.5	0.5	−2.5
	67	−1.5	−0.5	−0.5	−0.5
	79	−0.5	−1.5	0.5	−1.5
	24	0.5	−2.5	−0.5	−2.5
	26	1.5	−3.5	0.5	−3.5
	70	−1.5	−1.5	−0.5	−1.5
	77	−0.5	−2.5	0.5	−2.5
	28	0.5	−3.5	−0.5	−3.5
	23	1.5	−4.5	0.5	−4.5
	72	−1.5	−2.5	−0.5	−2.5
	74	−0.5	−3.5	0.5	−3.5
	33	0.5	−4.5	−0.5	−4.5
	76	−1.5	−3.5	−0.5	−3.5
	71	−0.5	−4.5	0.5	−4.5
	81	−1.5	−4.5	−0.5	−4.5

1-5 Sensitivity Increase with Hollow Cathode Lamp in A Pulse Mode

In preceding sections, the author described basic features of atomic magneto-optical rotation spectroscopy. It has been theoretically predicted and also experimentally proved that the spectral intensity of the radiation transmitted through the optical system in the Faraday configuration increases as the intensity of the source radiation increases. Murayama *et al.* [69] and Lolly *et al.* [70] also refer to this fact in another atomic magneto-optical phenomenon, the Voigt effect, applied to the trace determination of elements. Therefore, increasing the source energy should be essential for these methods to improve detection limits. For this purpose, Murayama *et al.* used a hollow cathode lamp boosted by r.f. power for trace analysis of elements by the Voigt effect [69]. The present author and his co-workers also discussed excitation by a combination of r.f. and d.c. plasmas in a hot graphite cathode lamp for the trace determination of cadmium by atomic emission spectroscopy [71]. For achieving this purpose with a conventional hollow cathode lamp, however, it seems suitable to intermittently enhance the source radiation by supplying the lamp with a succession of high-current pulses [72, 73], and to synchronously detect the transmitted optical energy.

In this section, the author wishes to describe analytical and spectral features of AMORS of Sb, Bi, Ag and Cu with a hollow cathode lamp operated in a pulse mode. The effect of the pulse modulation on the transient variation in the line profile of the source radiation was estimated by scanning the analytical line of copper Cu I 324.754 nm by means of a Fabry-Perot interferometer.

Fig. 1. Schematic diagram of the experimental arrangement: a = current stabilizing power supply; b = lamp-switching circuit; c = hollow cathode lamp; d = polarizing prism; e = lens; f = electromagnet; g = graphite tube atomizer and chamber; h = analyzing prism; i = prism monochromator; j = photomultiplier tube (HTV R928); k = D.C. pre-amplifier and voltage-sampling and holding circuit; l = pulse-generating circuit; m = audio frequency oscillator and n = strip chart recorder/recording oscillograph.

Apparatus

Figure 1 shows the schematic diagram of the experimental arrangement. the system composed of basically the same components as those used in the previous study except for the light source and associated electronics. They are listed in Table 1. Figure 2 depicts the block diagram of the electronic system constructed for this experiment. The electronic system consists of a lamp-switching circuit, a d.c. pre-amplifier, a voltage-sampling and holding circuit and a pulse generating circuit. From rectangular waves fed from an audio frequency oscillator, the pulse generating circuit generates pulses, P_L for switching the hollow cathode lamp current and those for sampling and holding the voltage converted from the photocurrents caused by the transmitted radiation due to the Faraday effect and by the blackbody radiation from the graphite

tube atomizer, i.e. pulses P_s and P_b respectively. The time correlation of pulses is shown in Fig. 3. When pulse P_L is in low voltage, the valve in the lamp-switching circuit is turned off and a large current is fed to the hollow cathode lamp from the current-stabilizing power supply. In practice, there existed a time lag between the pulse switching moment and the point of appearance of the spectral radiation in the lamp. Consequently, it is required for successfully registering the transient radiation that the sampling and holding pulse, P_s, is delayed so as to coincide in period with the plateau of the transient curve of radiation. When the switching pulse, P_L, is in high voltage, the valve is turned on, the discharge current is shunted through the valve and the hollow cathode lamp is turned off. Then, the photocurrent caused by the blackbody radiation is

Table 1. Specification of instrumentation

Monochromator	Hitachi EPU-2 prism monochromator
Entrance slit width	2 mm
Exit slit width	2 mm
Polarizer	Karl Lambrecht Glan-Taylor prism
Analyzer	Oyokodenken Rochon prism
Electromagnet	Constructed, Maximum magnetic field strength of 20 kG at a coil current of 10 A
Atomizer	Graphite tube atomizer of 2.5 mm i.d., 5 mm o.d. and 15 mm long
Detector	Photomultiplier tube Hamamatsu TV R928
Current regulating power supply for the lamp	Hitachi power supply for H_2-discharge lamp, modified
HV power supply for the detector	630 V fed by seven dry batteries of 90 V

Fig. 2. Block diagram of the electronic system: I = raw voltage corresponding to the photocurrent; I_b = blank voltage corresponding to the photocurrent induced by the blackbody radiation; $I_\perp$ = net voltage corresponding to the photocurrent induced by the transmitted radiation; S. & H.C. = voltage-sampling and holding circuit; C.S. = current-stabilizing power supply; L.S.C. = lamp-switching circuit; P.G. = pulse-generating circuit; OSC. = audio frequency oscillator; S = analogue-switching element, FET; C = capacitor for voltage-holding; F = Flip-Flop IC; M = mono-stable multivibrator IC, L.C. = voltage level converter; V = valve, 6RA3 × 4; H.C.L. = hollow cathode lamp; H.V. = dry batteries of 90 V; P_L = pulse for switching the lamp current; P_s = pulse for sampling the voltage $I_\perp$ and P_b = pulse for sampling the voltage I_b.

sampled and held in the capacitor, C_b, through the analogue switch, S_b turned on and off with the pulse P_b, and fed out through IC 1. IC 2 performs an analogue subtraction $I-I_b$ (i.e. the voltage corresponding to the raw photocurrent minus the voltage corresponding to the photocurrent caused by the blackbody radiation) for the removal of the bias voltage. When pulse P_s is in high voltage, the net voltage due to the Faraday effect is registered in the capacitor C_s and fed out by IC 3 to the recording system.

Fig. 3. Time correlation between switching pulses and variation in indicative parameters for the lamps: V_L = discharge voltage of the lamps, I_L = discharge current of the lamps and B.G.R. = background radiation from the graphite tube atomizer.

Unfortunately, however there often arises a problem associated with registering pulse noises of short time constant when using this box-car type of electronic system. This problem leads to an increase in the noise involved in the output voltage and to a decrease in the signal-to-noise ratio. In order to avoid it an averaging processess is applied during the period of sampling and holding the voltage, I_b, caused by the blackbody radiation. The fluctuation in voltage with time constant small enough compared to the sampling and holding period can be averaged by locating an appropriate time constant C_bR in the sampling and holding circuit.

In order to avoid rapid damage, the hollow cathode lamp should not be operated at the pulse discharge current except during the atomization process. However, the pulse mode requires a time of at least some 15 min for the radiance of the hollow cathode lamp to stabilize after the discharge current is turned on. This was overcome by operating the hollow cathode lamp at a low d.c. current of 2 mA during stages other than the atomization. By this means, the stabilization in radiance was established within about 15 s after the operation was changed over to the pulse mode.

Hollow cathode lamps of Sb (Hitachi), Bi (Hamamatsu TV), Ag (Hamamatsu TV) and Cu(Westinghouse) were used as the light source. The purge gas, argon, was introduced into the graphite tube atomizer and enclosing chamber at flow rates of 50 ml min^{-1} and

1.5 l min^{-1}, respectively. The atomization temperature was measured by an optical pyrometer (Tokyo Hokushin Denki). The magnetic field was calibrated versus the coil current of the electromagnet by a gauss meter (Yokokawa Denki).

A Fabry–Perot interferometer (Mizojiri Kogaku) was used for the evaluation of the hyperfine structure. The other components fitted to the interferometer were the same as those used previously, except the electronics. The electronic circuit constructed for the Faraday optical system was connected to the pre-amplifier and the hollow cathode lamp mounted on the Fabry–Perot interferometer assembly.

Standard solutions and procedure

Special grade reagents were used for the preparation of stock solutions. Test standard solutions were prepared by diluting the stock solutions immediately before use. Ten μl of test solutions was dispensed into the graphite tube atomizer by means of a micropipette (Muromachi Kagaku), dried at a temperature of 120°C for a minute and atomized at temperatures of up to 2000°C.

Operational characteristics of hollow cathode lamp in pulse mode

Figure 3 shows the time correlation of characteristic parameters of the Sb and Bi hollow cathode lamps with the logic pulses. As referred to above, there is a time lag between the point that the plateau of the radiation curve is reached and the point that the switching pulse, P_L, is applied to turn on the hollow cathode lamp. For this reason, the period of the sampling and holding pulse, P_s in the high voltage is adjusted so as to coincide within that of the plateau.

For the hollow cathode lamp of Sb, the rise time of the discharge current is longer and both of the discharge-initiating voltage and discharge voltage are higher than those for the Bi lamp. Parasitic waves are found on the rising slope of the discharge current curve. These phenomena indicate that the discharge impedance of the Sb lamp is higher than that of the Bi lamp and that the feed-back control of the current-stabilizing power supply is not rapid enough for establishing the regulated current. This is reflected in the rise behaviour of the photocurrent curves. The difference in impedance could be attributed mainly to the difference in geometry of the electrodes or inner diameter of the cathode between lamps of different manufacturers. The inner diameter of the Sb cathode is larger than that of the Bi cathode.

In addition to the difference in impedance, a difference in the sputtering behaviour of

Pulse rate	500	230	100	55	30	s^{-1}
Mean current	25	10.8	5.0	2.5	1.4	mA

Fig. 4. Effect of the pulse rate on the noise level in the voltage $I_\perp$: peak current is fixed at 200 mA and the noise mainly consists of the photopulses caused by the leak radiation due to the imperfect optical extinction of the polarizer and analyzer in the crossed configuration.

the elements also might be one of the factors to which the prolongation of the rise time of radiation must be attributed. For hollow cathode lamps of Cd and Pb (Hamamatsu

TV), the rise time was longer than that for the Bi lamp. The former lamps have a hollow cathode of almost the same dimension as that of the latter. Therefore, the time lag should not be attributed mainly to the difference in impedance but be related to the behaviour of the elements. In case of Cd and Pb, the spectral intensity decayed with a time constant similar to that for the rise, an effect which is not notable for the Sb radiation (Fig. 3). Therefore, in case of Sb, the time lag should be attributed principally to the difference in impedance rather than to that in the sputtering behaviour of the element.

To attain a higher signal-to-noise ratio in spectral response, a larger time sharing of the sampling and holding pulse is essential. For this purpose, two ways are available. One is to increase the pulse rate (number of pulses per second) and the other is a prolongation of the pulse duration. In either case, the noise components at high frequencies can be removed by an averaging process through the sampling and holding circuit. Figures 4 and 5 demonstrate these effects. A problem to be pointed out is that increasing the rate or the duration of the pulse discharge current increases the mean current for a defined peak current. The mean current should not exceed the maximum rating current. In addition to the mean current, the magnitude of the peak current is a main factor that dictates the shortening of the life of the hollow cathode lamps. For example, visible damage on the cathode surface of the Ag lamp was found after operating it with a peak current of 200 mA and a mean current of 10 mA for about half the period guaranteed for normal operation. Consequently, it is suggested that increasing the pulse rate or duration be associated with a lowering of the peak current in order to extend the life of the lamps under a condition of limited mean currents. Under such conditions, however, the intensity of the atomic line with high upper level and low transition probability such as Sb I 231.147 nm was not strong enough for the analysis, probably because of insufficient peak current for achieving a high excitation temperature.

Line profile study

The effect of pulse operation on the line profile of the source radiation was studied by interferometric scanning for Cu I 324.754 nm, which was intense and gave a typical

Short integration time Long integration time

Fig. 5. Effect of the time constant of the sampling and holding circuit on the noise level in the voltage I_b: short-time integration; $C_bR = 0.7\ \mu s$, $P_b = 20\ \mu s$, long-time integration; $C_bR = 200\ \mu sec$, $P_b = 2$ ms and the pulse rate is fixed at $300\ s^{-1}$.

hyperfine doublet [72, 73]. Figure 6 shows the typical interferogram of the line for the d.c. and pulse operations. In the latter mode, line broadening occurs, resulting in overlapping of the two hyperfine components. Figure 7 shows the time-resolved interferograms of the line. Line broadening is negligible at 100 μs but becomes significant at 300 μs after the discharge current is turned on. As discussed previously, line broadening affects the dependence of the transmitted intensity on the magnetic field strength. Figure 8 demonstrates the dependence for the two different modes. Compared to the curve for the d.c. mode, the transmitted intensity for the pulse mode is enhanced at higher field strengths. This is attributable to line broadening in the source radiation, i.e. the interaction region between the Zeeman components $\sigma^{\pm}$ in the absorption line and the source radiation is extended.

Fig. 6. Typical interferograms of the line Cu I 324.75 nm emitted from the hollow cathode lamp operated in the d.c. and pulse modes: the lower interferograms include averaging transient variations in the line profile.

Fig. 7. Time-resolved interferograms of the line Cu I 324.75 nm: figures indicate the time passed after the hollow cathode is turned on.

Fig. 8. Dependences of the transmitted intensity of the line Cu I 324.75 nm emitted from the lamp in the d.c. and pulse modes on the magnetic field strength pulse mode; pulse rate = 300 s^{-1}, peak current = 200 mA. d.c. mode: d.c. current = 10 mA. The introduced mass of Cu is 1.2 ng.

Analytical features

Detection limits (signal-to-noise ratio = 2) for the elements Sb, Bi, Ag and Cu are listed in Table 2 together with the operational conditions. The detection limits for Bi, Ag and Cu given in the pulse mode are one tenth of those given in the D.C. mode. Even larger amounts than 100 ng of Sb could not be detected in the d.c. mode. This is probably because the source radiation is not intense enough for detecting smaller amounts and atomic absorption is so deep for larger amounts that the source radiation is not allowed to pass. The effect of the pulse operation on the enhancement in sensitivity is notable for this case. As described above, the rise in excitation temperature caused by the increase in discharge current is determining for the enhancement in source intensity of a line with high upper level energy and low transition probability. This can be also applied to the case of Bi I 223.061 nm.

The calibration curve gave the square law dependence on the mass of elements up to about 10^3 times the detection limits. However, the curve bent for larger amounts. This could be attributed to the same cause as that suggested in the previous paper [5], i.e. the interaction between the source radiation and $\sigma^{\pm}$-components of the absorption line in the wing-to-wing fashion.

For Sb, Bi and Cu the relative standard deviations found in the pulse mode were roughly the same as those found in the d.c. mode and did not exceed *ca.* 7% for 5–10 repeated measurements with an amount equal to ten times the detection limit. For Ag, however, the reproducibility in the pulse mode was poorer (~15%) than that in the d.c. mode. This is partly due to the narrowing of the beam of source radiation. Localizations or inhomogeneities in the atomic cloud generated in the graphite tube atomizer manifest themselves in the narrowed beam and this may lead to a poorer reproducibility. To confirm the narrowing, we measured the diameter by inserting a needle tip of

Table 2. Detection limits

Element	Atomic temperature (°C)	Wavelength (nm)	d.c. mode				Pulse mode		
			i (mA)	D.L. (pg)	H (kG)	i_p (mA)	P.R. (μs)	P.W. (μs)	D.L. (pg)
Sb	2000	231.147	20	N.D.	5.0	200	300	400	500
Bi	2000	306.772	15	500	3.5	200	1000	150	50
		223.061	15	N.D.	10.0	200	1000	150	500
Ag	1800	328.068*	15	20	6.0	200	300	300	2
		328.289*							
Cu	1800	324.754	20	30	2.5	300	300	530	3

i: D.C. discharge current of the hollow cathode lamp.
D.L.: detection limit (S/N = 2).
H: magnetic field strength.
i_p: peak discharge current of the hollow cathode lamp.
P.R.: rate of the discharge-current pulses.
P.W.: width of the discharge-current pulses.
N.D.: not detectable.
* The lines are not separated because of the large band pass of the monochromator.

the micropipet through the sample injection hole of the graphite tube atomizer, and observed the reduction in the spectral energy. The beam filled the atomizer of 2.5 mm i.d. in the d.c. mode while the beam diameter was reduced to less than about 1.5 mm in the pulse mode. Visibly the red plasma of the filling gas neon in the hollow cathode was narrowed in the pulse operation. This might be associated with a plasma pinch effect

caused by the condensed rush current in the hollow cathode. In case of Ag, better reproducibility was achieved when the hollow cathode was set out of focus in the graphite tube atomizer although the detection power worsened because of the optical energy loss.

A hollow cathode lamp operated in a pulse mode was quite effective for improving the detection limits of atomic magneto-optical rotation spectroscopy of the elements Sb, Bi, Ag and Cu. The dependence of the transmitted intensity on the magnetic field strength showed the presence of novel line crossings in the line Bi I 306.772 nm. This coincides essentially with the theoretically calculated pattern of Zeeman splitting in the line. Line broadening in the source radiation caused by the pulse operation presented such a useful effect that the transmitted optical energy was increased in stronger fields, leading to improved detection power.

1-6 Approach to Direct Atomization and Practical Application

Atomization of solid samples by means of an electrothermal atomizer appears attractive in that the complicated wet digestion procedure can be omitted, and consequently in that the size of raw samples required for analysis is very small and the possibility of contamination and/or loss of elements can be minimized. In the direct atomization, however, the most serious problem to be pointed out is background absorption and scattering of the source radiation, which are encountered in atomic absorption spectrometry (AAS) and atomic fluorescence spectrometry (AFS), respectively. These are ascribed mainly to non-atomic species generated in the electrothermal atomizer at high temperatures. Recently, Koizumi *et al.* have successfully applied the Zeeman effect to AAS for correcting the background absorption [74-76]. For correcting background scattering in AFS, however, no efficacious technique has been proposed, though Koizumi *et al.* alluded to a possibility to apply the Zeeman effect also to AFS [77].

In the early work (Sec. 1-3), the atomic magneto-optical rotation spectroscopy proved to have such an advantage that it was free from background scattering. It was pointed out that the negative interference or reduction in the intensity of the transmitted radiation was caused by non-atomic species. However, this problem was overcome by a correction method which involved a comparison between the magnitude of optical energies transmitted through the system, when a pair of polarizers were mounted in the crossed and parallel configurations. Two types of optical system were tentatively constructed and their performance was evaluated by determining trace amounts of cadmium in synthesized samples containing starch as a matrix to evolve interfering non-atomic species. Another improved version of correction system also was constructed and used for the practical applications.

Three kinds of samples containing typical matrix, i.e., NBS Standard Sample Orchard Leaves SRM 1571, volcanic ashes from Ontake Volcano and human blood samples, were analyzed and the results were cross-checked. By this means, the precision and accuracy were evaluated.

1-6-1 Principle of correction method

As was discussed in previous sections, the intensity of radiation transmitted through the Faraday configuration is expressed as follows if the number of atoms in the light beam is small enough

$$I_{\perp} \propto (NLB)^2 I_0 \int_w \rho'(k) F(k, H)^2 \, dk, \tag{1}$$

where N is the concentration of atomic vapor, L its optical path length, B the transition probability, I_0 the intensity of the source radiation, w the spectral bandpass of the monochromator, $\rho'(k)$ the line profile function of the source radiation, $F(k, H)$ the Faraday function, H the magnetic field strength, and k the angular frequency.

If there exist non-atomic species in the atomizer that absorb and scatter the incident light, the intensity can be approximately expressed by the following equation

$$I_{\perp} \propto (NLB)^2 I_0 e^{-\alpha_b L_b}, \tag{2}$$

(for a definite H and $\rho'(k)$), where α_b is the apparent absorption coefficient for the non-atomic species and L_b its optical path length. For AFS, the intensity of the re-emitted radiation I_{FL} can be approximated by the following equation

$$I_{FL} \propto (KNLB + K_b N_b L_b) I_0 e^{-\alpha_b L_b}, \tag{3}$$

where K is a constant involving the quantum yield in the fluorescent process, K_b a constant involving the quantum yield in the scattering process and N_b the concentration of non-atomic species. The second product in parentheses corresponds to the positive background radiation. In the Faraday configuration, this is blocked by the analyzing prism unless depolarization occurs when the incident radiation passes through the non-atomic cloud.

There is such a possibility that the standard addition method enables us to remove the negative interference corresponding to the exponential term in equation (2). If the unknown concentration is denoted as N_0, the calibration curve for the standard addition method using atomic Faraday spectroscopy is given by the following equation

$$\sqrt{I_{\perp}} \propto (N + N_0) LB \sqrt{I_0 e^{-\alpha_b L_b}}. \tag{4}$$

At the intersecting point on the axis of concentration, $-N_0$ should be equal to N. Thus, the standard addition method yields the unknown value, independently of the presence of non-atomic species. On the other hand, for AFS the expression is modified as follows

$$N = -\left(N_0 + \frac{K_b N_b L_b}{KLB}\right). \tag{5}$$

In this case, the positive background causes an error dependent on the concentration of non-atomic species. Therefore, it is expected that the negative interference effect caused by non-atomic species can be removed in both atomic Faraday spectroscopy coupled with the standard addition method and AFS coupled with the standard addition method, but the positive background is inevitable in AFS.

In the routine analysis, however, the correction method is suitable for the removal of the negative interference in atomic Faraday spectroscopy in that it can perform the correction in a single measurement while the standard addition method requires various measurements.

If the atomic absorption is small enough, the intensity, $I_{\parallel}$, transmitted when the plane of polarization of the polarizer is parallel to that of the analyzer can be expressed as follows:

$$I_{\parallel} \propto I_0 e^{-\alpha_b L_b} \int_w \rho'(k) dk \tag{6}$$

As the integral term is unity,

$$I_{\parallel} \propto I_0 e^{-\alpha_b L_b} \tag{7}$$

If we take a ratio of $I_{\perp}$ to $I_{\parallel}$, defined as T_c, then

$$T_c \propto (NLB)^2 \int_w \rho'(k) F(k,H)^2 dk \tag{8}$$

Therefore, under the condition of a constant strength magnetic field and a definite line profile of the source radiation, the corrected term T_c becomes

$$T_c \propto (NLB)^2 \tag{9}$$

and hence

$$\sqrt{T_c} \propto NLB \tag{10}$$

Thus, the square root of the corrected term is proportional only to the number of atoms in the light beam and is independent of the presence of background components and variation in the source intensity.

1-6-2 Correction systems

To embody the principle stated above in a rapidly responding system, two kinds of optics were tentatively constructed and compared. One of them, illustrated in Fig. 1, incorporates a Glan-type prism with an escaping window on the lateral face (Karl Lambrecht Co. Ltd.) as the analyzer and two photomultiplier tubes behind the exit slit of the monochromator. The other optical elements, the electromagnet, the electrothermal atomizer and the polarizer are the same as those used in the previous experiment. The analyzer passes the ordinary ray along the optical axis and the extraordinary ray at an angle of about 24° to the axis in the ultraviolet region. The polarizer and the analyzer were set in such a fashion that the ordinary ray coincided with $I_{\perp}$ and the extraordinary ray with $I_{\parallel}$. The separated radiations were detected by separate photomultiplier tubes (Hamamatsu TV Co. Ltd., R928). The source radiation was chopped at a frequency of 285 Hz by a mechanical chopper (Varian-Techtron Co. Ltd.) located between the source and the polarizer. The resulting photocurrents were fed to the electronic system, the

Fig. 1. Schematic diagram of static system for correction of energy loss. A, EDL and microwave cavity; B, chopper; C, lens and polarizer; D, electromagnet and electrothermal atomizer; E, monochromator; F, analyzer (Glan prism with escape window); and G, photomultiplier tube (HTV R928).

Fig. 2. Circuit diagram of electronic system for the static system.

circuit diagram of which is shown in Fig. 2. Each of the photocurrents was converted into voltage and amplified through an a.c. amplifier. The coupling capacitor between the photomultiplier tube and the amplifier removes the d.c. voltage resulting from the black-body radiation emitted by the electrothermal atomizer. The operational amplifier employed was a bi-FET IC, LF356 (Intersil Co. Ltd.), the high input impedance of which allowed it to be the load of the photomultiplier tube. Because of the large difference in energy between $I_\perp$ and $I_\parallel$, the gain factor for the former was set higher (100) than that for the latter (10). Following a buffer amplifier, each of the a.c. signals was fed through a band-pass filter tuned to a frequency of 285 Hz with a Q-factor of 10 and rectified by an ideal diode circuit. The resulting d.c. signals were operated upon by a programmable multifunction analogue module (Analog Devices Co. Ltd., Model 433 J) according to the equation

$$V_{\text{out}} = \frac{10}{9} \times V_{\text{y}} \left(\frac{V_{\text{z}}}{V_{\text{x}}}\right)^m \tag{11}$$

were $m = R_2/(R_1 + R_2)$. Let $V_z \propto I_\perp$, $V_x \propto I_\parallel$, $m = ½$ and $V_y = 0–9$ V for adjusting the over-all gain factor. Then, $V_{\text{out}} \propto \sqrt{I_\perp/I_\parallel}$ and $V_{\text{out}} \propto NL$. Therefore, if the strength of magnetic field and the profile of the absorption line are defined, the output voltage varies proportionally only with the number of atoms in the light beam. However, a problem arose in that the monochromator partially depolarized the incident radiation. This caused a bias current even if the atomic vapour was absent. To offset this current, an additional circuit was inserted between the rectifier and the function module. Consequently, the output voltage is modified as in equation (12):

$$V_{\text{out}} = \frac{10}{9} \times V_{\text{y}} \left(\frac{k_1 I_\perp - k_2 I_\parallel}{I_\parallel}\right)^m \tag{12}$$

where $k_2 I_\parallel$ is the additional term for cancelling the voltage resulting from the depolarization. When atoms are absent, the numerator is pre-set to zero.

Fig. 3. Schematic diagram of time-sharing system for correction of energy loss. A, EDL and microwave cavity; B, modulation system; C, electromagnet and electrothermal atomizer; D, analyser and lens; E, monochromator; and F, photomultiplier tube (HTV R928).

The alternative system is illustrated in Fig. 3, the details of its mechanical modulator are shown in Fig. 4 and the circuit diagrams of the gating and signal processing electronic circuits in Fig. 5. The mechanical modulator consists of a disc rotor for chopping the source radiation and a holder for the polarizer. The holder is rotated by a synchronous motor at 3600 rev min^{-1} through a belt drive and the disc linked to it by gears. The correlation in time sharing is shown for the detected radiations *versus* the rotational angle of the plane of polarization of the polarizer in Fig. 6. At positions a and c the rotor blinds the detector from the source radiation and only black-body radiation from the electrothermal atomizer falls on the detector. Synchronously, an analogue switch S_b is closed and the voltage corresponding to the black-body radiation is sampled and stored in the capacitor C_b. At the instant b, the source radiation is allowed to pass through an aperture in the rotor and reach the polarizer. As the polarizer and the analyser are in the crossed configuration at this moment, the detected energy is the magnetically rotated radiation, $I_\perp$, plus the black-body radiation, I_b. The following operational amplifier subtracts the voltage I_b from this voltage, giving the output voltage as the net energy of the magneto-rotation. Concurrently, a switch $S_\perp$ operates and the voltage is sampled and held in the capacitor $C_\perp$. At moment d, the rotor allows the source radiation to reach the polarizer and the plane of polarization of the polarizer is now parallel to that of the analyzer, so that the resulting voltage is the reference voltage, $I_\parallel$, plus the voltage owing to the background radiation, I_b. After subtracting I_b, the net voltage $I_\parallel$ is sampled and held in the capacitor $C_\parallel$ by closing and opening the analogue switch $S_\parallel$. The sequence of operations is repeated during the remaining half cycle. The resulting signals $I_\perp$ and $I_\parallel$ are fed to the same function module as that used in the preceding system.

Fig. 4. Schematic diagram of modulator in the time-sharing system. E, EDL; L, small lamp; D, rotatory disc; PH, phototransistor; G, gear system; P, polarizer; S, stripes for synchronisation; and M, motor.

In the preliminary experiment, the triggering pulse for the synchronous operation of the analogue switches was generated by detecting radiation from a small lamp after passing through holes bored on the rotor. However, the stability of the pulses was not satisfactory, partially attributable to fluctuations in the gear system. To improve the stability, the radiation from the small lamp was detected by a phtotransistor after reflection by stripes marked on a drum mounted on the axis of the polarizer. Another pulse was taken to define the sequence of the operation of the analogue switches. As the photocurrent is significantly different in magnitude between the parallel and crossed configuration, the gain of the preamplifier is synchronously altered by switching the resistance in the feedback network.

Fig. 5. Circuit diagrams of (*a*) analogue and (*b*) digital electronic circuit for the time-sharing system. C, capacitor; *P*, switching pulse; and S, switch.

The two systems presented similar results from the standpoint of correction ability. However, in the first system, probably because of the depolarizing property of the monochromator prism, a considerable leak of energy (about 2% of the

incident radiation) was observed in the crossed configuration. This generated a bias photocurrent in the photomultiplier tube intermediate in form between the continuous and pulse modes. The continuous current was offset electrically according to equation (12) but the noise level on the base line was increased owing to the pulse current. The following results therefore relate mainly to the time-sharing system.

Optimization of Switching Pulses

Figure 6 shows a trace of the photocurrent (V_t) displayed on a cathode-ray oscilloscope (Iwasaki Tsushin Co. Ltd.) and synchronized with those of the switching pulses for the analogue gates of S_b, $S_\perp$ and $S_\parallel$. To offset the blank signal due to the black-body radiation, the switching pulses P_b were set as close to $P_\perp$ and $P_\parallel$ as possible; the time interval between the pulses of P_b and $P_\perp$ or $P_\parallel$ was synchronized to be 1 ms.

Fig. 6. Traces of photocurrent and pulses for analogue switching. V_t, Photocurrent converted into voltage; $P_\perp$, switching pulse at crossed configuration; $V_\perp$, voltage sampled and held at crossed configuration; $P_\parallel$, switching pulse at parallel configuration; $V_\parallel$, voltage sampled and held at parallel configuration; P_b, switching pulse for sampling black-body radiation; V_b, voltage of black-body radiation sampled and held; and P_g, pulse for switching gain of pre-amplifier.

Figure 7 is the oscilloscope trace of the $I_\perp$ signal as a function of the width of the switching pulse. Up to a width of 50 μs, no significant change in noise level was found. For greater widths, however, the noise level increased progressively. This increase may be attributed to the wider pulse sampling the transmitted radiation at moments when the polarizer and analyzer are incompletely crossed, and to some vibration in the mechanical system of modulation. Up to a 50-μs pulse width no variation in the energy of the stored signals was found when atomizing 25 pg of cadmium at 1800°C. Taking into account the slew rate of the operational amplifier, we determined the optimum pulse width to be 25 μs.

Fig. 7. Oscilloscope trace of $I_\perp$ signal to show dependence of base-line noise on width of switching pulse with crossed polarizer configuration.

Signal to Noise Ratio

There remains, however, a problem inherent in the time-sharing system. As the system involves a "box-car" circuit, the photocurrent that is sampled and held has a value corresponding to the moment for which the gate is open. Most of the noise included in the output voltage can be attributed to the pulses generated in the photomultiplier tube. When the radiation does not reach the photomultiplier tube, the pulses are assignable to thermal noise. When the number of photons is small, the photocurrent becomes a series of pulses. In this instance, the sample and hold circuit leads to significant variations in the peak response. In either instance, a short current pulse is held and converted into a longer voltage pulse. This leads to a disadvantage in that it is difficult to remove the noise by a circuit of low pass filter. The problem of the thermal noise can be reduced by cooling the photomultiplier tube.

Improved Correction System

Figure 8 shows the schematic diagram of the experimental arrangement. The optical system is slightly different from the static one constructed above. Owing to the optical activity of the dispersing prism in the monochromator,

Fig. 8. Schematic diagram of the experimental arrangement. (A) hollow cathode lamp, (B) Glan-type prism, (C) lens, (D) electromagnet, (E) graphite tube atomizer and atomization chamber, (F) Rochon prism, (G) iris diaphragm, (H) prism monochromator, (I) plane mirror, (J) photomultiplier tube (R955), (K) photomultiplier tube (R306), (L) a.c. preamplifier, (M) bandpass filter amplifier, (N) phase-sensitive rectifier, (O) off-set amplifier, (P) operational amplifier for dividing and square root processing, (Q) strip chart recorder, (R) pulse generator and (S) current stabilizing power supply.

the extraordinary and ordinary rays could not be perfectly distinguished in the previous system. In order to avoid this, a Rochon prism was used as the analyzer and located in front of the entrance slit of the monochromator. The other optical elements, the electromagnet and the graphite tube atomizer are the same as those used in the previous experiment. The Rochon prism conducts the ordinary ray along the optical axis and the extraordinary ray at an angle of *ca.* 3° with the optical axis for the radiation in u.v. region. The polarizer and analyser were set so that the plane including the separated rays was parallel to the direction of the entrance slit, and that the ordinary ray coincided with $I_{\perp}$ and the extraordinary ray with $I_{\parallel}$. The rays dispersed emerging from the exit slit are focussed on a plane mirror located in the detector chamber. The plane mirror is declined at an angle of *ca.* 30° toward the exit slit. The extraordinary ray is reflected by the mirror and received by a photomultiplier tube (Hamamatsu TV R306). The ordinary ray goes straight on and reaches another

photomultiplier tube (Hamamatsu TV R955).

A hollow cathode lamp of Cd used as the light source was operated with a current pulsed at a frequency of 1 kHz by a current-regulating power supply. Each of the photocurrents resulting from the photomultiplier tubes is converted into a voltage, amplified by an AC pre-amplifier and fed to an electronic system constructed for this study. The electronic system consists of a bandpass filter tuned at a frequency of 1 kHz, a phase-sensitive rectifier and an operational amplifier for division and square root processing. The photomultiplier tube (R955) yielded a bias current which must be principally attributed to the imperfect extinction (extinction ratio of *ca.* 10^{-4}) inherent in the polarizing prisms. In order to off-set the bias current, a subtracting circuit is connected between the phase-sensitive rectifier and operational amplifier.

Effectiveness of Correction with Constant Optical Rotation

The corrective ability was estimated using 0.05 mm thick film of low-density polyethylene that was stretched unidirectionally to produce optical activity. The film was mounted between the pole pieces of the electromagnet and, by means of its optical activity, allowed a constant signal to be transmitted through the optical system. The microwave power supplied to the cadmium EDL was varied from 100 to 70 W. Figure 9 shows traces of the reference signal, $I_{\parallel}$, and of the computed signal, $\sqrt{T_c}$, when cigarette smoke was introduced between the pole pieces. The peaks on the reference signal trace correspond to the loss of energy due to scattering by the smoke; these peaks, however, do not appear on the computed signal traces. These results illustrate three important aspects for practical analysis:

(1) the system does not respond to radiation scattered by non-atomic species;

(2) the system corrects for the influence of changes in source intensity;

(3) the system corrects for the reduction in incident and transmitted energy arising from background absorption.

The noise on the corrected signal increased as the source intensity decreased. This effect is attributable to the decrease in the signal to noise ratio in the numerator and denominator of equation (12), due to the reduction in the radiation output of the lamp.

Fig. 9. Traces showing correction for energy loss and variation in intensity of source radiation. Arrows indicate the introduction of cigarette smoke.

Correction in Electrothermal Atomization

Figure 10 shows oscilloscope traces of the corrected response for pyrolysis of different amounts of starch at the atomization temperature of 1800°C. As no ashing procedure was applied, a concentrated cloud of background species was

Fig. 10. Oscilloscope traces of the corrected response for pyrolysis of different amounts of starch at the atomization temperature of 1800 °C, showing the background scattering. 1, No starch; 2, 2.5 μg of starch; 3, 5 μg of starch; and 4, 10 μg of starch.

generated in the electrothermal atomizer. In practice, the reference signal $I_{\parallel}$ was rapidly reduced as shown in Fig. 10, but no background signal appeared on the $\sqrt{T_c}$ trace, except an increase in the noise level. Partly because of imperfection in the transient response of the electronic circuit for the static system, an erroneous signal equivalent to 5 pg of cadmium was generated by the correction system when the loss of the incident energy reached 99%. From this point of view, the "box-car" circuit employed for the time-sharing system gave better results than the combination of band-pass filter and rectifier employed in the two-detector system.

Figure 11 shows oscilloscope traces of the response of the system to 50 pg of cadmium in solutions to which starch was added in various concentrations to produce background absorption. After drying at 120°C for 1 min, 5 μl of the solution were atomized at 1800°C without ashing. The traces of the reference signal, $I_{\parallel}$, [Fig. 11 (*c*)] are a measure of the energy loss due to the resulting background component and the absorption by atomic cadmium. When starch was present in a concentration of 0.3%, only 5% of the incident radiation was transmitted by the smoke generated by the pyrolysis of starch. The base-line drift is assigned to the variation in the source intensity. The traces in Fig. 11 (*b*) are the uncorrected response corresponding to $I_{\perp}$, and it is obvious that the resulting smoke reduces the transmitted intensity and causes the negative interference. In Fig. 11 (*a*) it can be seen that the use of the function $\sqrt{T_c}$ buffers the interference.

Fig. 11. Correction of energy loss and variation in intensity of source radiation for electrothermal atomization. 1, 50 pg of cadmium; 2, 5 μg of starch added; 3, 10 μg of starch added; and 4, 15 μg of starch added. See text for explanation of (*a*), (*b*) and (*c*).

1-6-3 Practical application

With the use of the improved correction system stated above, trace amounts of lead, manganese and chromium in some samples were determined by direct atomization. As model samples in complex matrices, NBS Standard Sample Orchard Leaves SRM 1571, volcanic ashes emitted from Ontake Volcano and human blood samples were chosen. The experimental conditions were basically the same as the optimum determined in Sec. 1-4.

Standard solutions and samples. A lead stock solution of 1000 μg ml^{-1} was prepared by dissolving lead metal in a minimum volume of a 6 N nitric acid solution and diluting the solution to one litre with distilled and deionized water. All test solutions were prepared by diluting the stock solution and adjusting the acidity to 0.1 N with nitric acid immediately before use. Stock and test solutions of manganese and chromium were also prepared as nitrates solution acidified with nitric acid.

The NBS Orchard Leaves SRM 1571 was kept tightly closed and stored in a cool and dark place. In order to avoid any contamination in the drying process, the sample weight was evaluated by such a process that the percentage of weight loss was determined by drying a dummy portion of the Orchard Leaves as prescribed by the National Bureau of Standards, another raw portion was weighed prior to the analysis, and its weight was translated into the dry weight. Human blood samples containing an anti-coagulation reagent were stored in an electric refrigerator. In another laboratory, the lead content has been determined by graphite furnace-AAS with a D_2-lamp background correction (Nippon Jarrell Ash Co., AA-8200). The volcanic ash samples were those resulting from the 1979 Eruption of Ontake Volcano. It is interesting to note that the Eruption was most unexpected, as the Ontake Volcano has preserved silence for a period of more than 10,000 years.

Pb: For calibration, 10 μl of the standard solution were taken by a micropipette (Muromachi Kagaku Co.), transferred into the graphite tube atomizer, dried at a temperature of 120°C for 1 min and atomized at a temperature of 1800°C.

About 75 mg of the Orchard Leaves were weighed and transferred into a cylindrical glass vessel of 50 ml volume. Thirty ml of distilled and deionized water or standard solution were added. The vessels were tightly plugged and floated in a 500 ml beaker containing an appropriate volume of water. This beaker was put in an ultrasonic bath supplied with an ultrasonic power of *ca.* 100 W at a frequency of 29 kHz and allowed to stand there for 30 min.

The resulting suspension of samples was taken into the tip of the micropipette. Any suspension adhering to the outer surface of the tip was wiped off with a clean sheet of tissue paper for laboratory use. The water in the ultrasonic bath was replaced by water at room temperature before it was heated by the ultrasonic power to a temperature of about 45°C.

This was done for protecting the ultrasonic vibrating element from becoming overheated and also for minimizing pipetting errors caused by volume expansion of the liquid. The suspension was injected into the graphite tube atomizer, dried at a temperature of 120°C for 1 min and atomized at a temperature of 1800°C. For cleansing purposes, the graphite tube atomizer was heated to a temperature higher than the atomization temperature prior to every run.

One ml of distilled and deionized water or standard solution was added to 1 ml of the human blood sample. Ten microlitres of the diluted blood solution were introduced by means of the micropipette. The portion of the sample solution adhering to the outer surface of the tip was wiped off in the same way as in the analysis of the Orchard Leaves. This procedure is essential especially in the analysis of blood samples. Without

this, the edge of the sample injection port of the graphite atomizer was contaminated by adhering sample and even a thin layer was formed there when the tip was inserted through the port. This resulted in a poorer reproducibility. Probably because the modes of the contamination are not defined, the atomic cloud generated from the bottom of the graphite tube atomizer could be irregularly perturbed by that from the injection port. The sample solution pipetted into the graphite tube atomizer was dried at a temperature of 90°C for 90 s, pre-charred at 520°C for 50 s, charred at 670°C for 50 s and atomized at 2000°C. The graphite tube atomizer was heated to a higher temperature for cleansing purposes, prior to every run. When a series of analyses was carried out, a time interval of about 3 min at least was required for cooling the atomizer after heating. Without this, foam of blood was formed when the sample solution was injected. This caused spattering of blood droplets to undefined sites of the internal face of the graphite tube atomizer resulting in the poor reproducibility.

About 0.3 g of the raw sample of volcanic ashes was weighed, transferred into a cylindrical glass vessel of about 50 ml volume. Thirty ml of distilled and deionized water were added to the ashes. This was stirred by a magnetic stirrer revolving at a constant frequency for 5 min. While the sample was stirred, 10 μl of the resulting suspension were taken into the tip of the micropipette. Ash particles adhering to the tip face were wiped off. The suspension introduced into the graphite tube atomizer was dried at a temperature of 120°C for 60 s and atomized at a temperature of 2000°C. Prior to every run, the graphite tube atomizer was cleansed at a higher temperature.
Mn: Calibration was made in the same fashion as that for Pb. The atomization temperature was 1900°C. Volcanic ashes of 82.7 mg were dispersed in 300 ml of distilled and subsequently deionized water by means of a magnetic stirrer. While stirring, 10 μl of the resulting suspension was introduced into the graphite tube atomizer by means of the micropipette, dried at ca. 120°C for a minute and atomized at 1900°C. The analytical line was Mn I 279.482 nm (triplet).
Cr: Calibration was made in the same mode as that for Mn and Pb. The atomization temperature was 2000°C. Orchard Leaves of 1.31 g was dispersed into 20 ml of a nitric acid of 0.7 N, by a magnetically vibrating mixer (Yamato Kagaku Co. Ltd.). Ten μl of the suspension was taken into the micropipette from the vibrating mixer, transferred into the graphite tube atomizer, dried at 200°C for a minute, charred at 350°C or 700°C for a minute and atomized at 2100°C. Volcanic ashes of 0.41 lg were dispersed into 30 ml of a 0.4 N nitric acid and analyzed in the same fashion as that for Orchard Leaved. The analytical line was Cr I 357.87 nm.

Characteristics of the analytical process and correction

Pb: Figure 12 demonstrates typical peaks of $I_{\perp}$ and $I_{\parallel}$ for the atomization of the Orchard Leaves. The process included no charring process. From the absorption peak $I_{\parallel}$, it is found that the peaks corresponding to the pyrolysis and atomization are separated from each other during the rise of the atomizer temperature to equilibrium. This indicates that the correction method is not necessarily required for this case. A similar separation phenomenon was observed also in the analysis of a synthetic sample solution containing a starch matrix at concentrations up to 2.5%. In the analysis of cadmium in the same matrix, non-atomic species generated from the matrix interfered with the atomization peak. The difference should be attributed to the higher atomization temperature of lead.

In the analysis of human blood, however, the interference or energy loss in the transmitted radiation was so serious that the source radiation scarcely passed through the optical system. This would be partly because the matrix contents are fairly large and

partly because the pyrolysis of proteins in the sample matrix yields non-atomic species such as NO, which is stable at the atomization temperature and has a strong absorption band (γ-band) in the u.v. region. In order to reduce the interference, charring was inevitable. When the charring process is applied to the analysis of elements whose salt is volatile, the optimization of the charring temperature is critical to avoid loss of elements. Figure 13 shows the dependence of the transmitted intensity on the charring temperature in the analysis of human blood. At temperatures below 500°C, the loss of optical energy is significant. This is ascribed mainly to non-atomic species (typically smoke) resulting from the pyrolysis of blood. Also at higher temperatures beyond 700°C, the optical energy decreases drastically. This reflects the loss of lead in the charring process. In a preliminary experiment, a single charring process was performed at compromise temperatures between 510 and 670°C. However, a prolonged time was required for the completion of charring at lower temperatures. On the other hand, charring at higher temperatures led to a poor reproducibility. Because of the low thermal conductivity and high viscosity of blood, charring appears to occur locally and portions of the sample might be spattered to undefined positions in the graphite tube atomizer. In order to overcome this, a double-stage charring process was introduced. The first is carried out at a temperature of 520°C for 50 s and the second at a higher temperature of 670°C for 50 s. In practice, however, even the double-stage charring process could not completely remove the formation of non-atomic species during the

Fig. 12. Typical peaks of $I_{\perp}$ and $I_{\parallel}$ for NBS Orchard Leaves SRM 1571. O.L. = Orchard Leaves.

Fig. 13. Dependence of the transmitted intensity on the charring temperature for human blood.

atomization process. The correction method demonstrated an effective capability for this case. Figure 14 shows a typical example. The upper and lower curves depict the absorption signal and the corrected signal T_c respectively. The curves on the left-hand side show a typical case where the sample was skilfully charred and background absorption did not interfere with the atomization peak, whereas the curves on the right-hand side illustrate the contrary case. By comparing the absorption and corrected curves for the two cases, it is seen that the correction is successfully applied to the atomization peak. When the transmitted energy decreases, the noise level increases. The noise consists principally of the thermal dark pulses from the photomultiplier tube. For the low transmittance, the relative magnitude of the fluctuations in the photocurrents corresponding to $I_\perp$ and $I_\parallel$ increase and result in an increase in the noise level on the T_c curve. The increased noise on the tail part of the atomization peak arises partly from the increased number of photopulses induced by unmodulated blackbody radiation emitted from the graphite tube atomizer. In order to lower the detection limits, it is essential to reduce the noise pulses relative to the magnitude of the transmitted optical energy. One of the possible ways is to use an intensive light source.

In the analysis of the volcanic ashes, a trace of background absorption appeared on the front slope of the atomization peak. This might be caused by the refractory particles resulting from the ashes that float in the graphite tube atomizer and scatter the radiation from the light source. In practice, the floating particles were visible through the aperture along the optical axis when the sample was atomized. At the same temperature as in the atomization of the Orchard Leaves, tailing of the atomization

Fig. 14. Two typical cases of correction in the analysis of human blood.

peak was hardly observable and the appearance time of the atomization peak almost coincided with that in the analysis of the standard solutions. This suggests that the particle size (almost smaller than 100 mesh) is small enough for thermally extracting lead components from the sample matrix.

Mn: Because the sample matrix was of silicates, the background absorption was negligible. When the samples was prepared by dispersing 82.7 mg of volcanic ashes in 200 ml of distilled and subsequently deionized water, the peak of the transmitted radiation was broken into three peaks. For 82.7 mg/100 ml, the peak was broken into four peaks. For 82.7 mg/300 ml, the peak was single. This may be attributed to the following reason. When the large sample mass is introduced,

the sample particles are piled up in a thick layer. Since the sample contains silicates of a low thermal conductivity, compounds of manganese is fractionally distilled on the atomization process.

Cr: There arised a serious memory effect in the atomization of test solution of chromium by the graphite tube atomizer. In order to avoid this, a similar size glassy carbon tube (Tokai Carbon Co. Ltd.) was employed as the atomizer. Despite the decrease in sensitivity due to the relatively inert surface, compared with the graphite surface, the glassy carbon tube atomizer did not cause any memory effect. Its low thermal conductivity (ca. a fifth of that of graphite), however, tends to cause the fractional vaporization of sample compositions. The background absorption for Orchard Leaves could be more easily removed by the charring process at a higher temperature of 700°C than that for lead, because the lower volatility of chromium. For a comparison purpose, a lower charring temperature of 350°C was employed to evolve the background absorption. The transmitted intensity was decreased by the background absorption and became about 44% of the intensity at 700°C. Because of the low volatility of chromium, non-atomic and atomic species must be clearly fractionated than those for lead. The inconsistency is attributable to the larger sample size introduced because of the lower contents of chromium in the Orchard Leaves. As in the case of lead analysis in human blood samples, the decrease in the transmitted intensity caused by background absorption was successfully corrected by the correction system (see Table 1). Thus, even in the analysis of elements with high volatility, the correction is effective for such a case that charring at lower temperatures is inevitable when large amounts of samples must be introduced because of the low concentration of the elements of interest and the possibility of element loss is increased in the charring process at high temperatures for a prolonged time. In the atomization of the volcanic ashes, the background absorption was negligibly small.

Analytical results and problems

Analytical results are listed in Table 1. The inaccuracy for the Orchard Leaves is +0.67% in terms of relative error. If we confine ourselves to this point, we may conclude that there is fair agreement. However, the precision amounts to 19.2% in terms of r.s.d. The resulting fluctuations are attributable to those both the sample introduction and instrumental measurement. In order to estimate the former, the Orchard Leaves suspension taken into the tip of the micropipette was weighed by a microbalance (Mettler ME-30). The precision was 14.3% in terms of relative standard deviation for ten repeated runs. The instrumental precision was, at the most, 7% when the standard solutions were introduced. Therefore, it can be seen that the major cause for the fluctuations must be ascribed to the poor reproducibility in taking the sample suspension. The problem should be more serious when the suspension contains particles of larger size.

For human blood, the inaccuracy amounts to 17.7% at the most in terms of relative error when the results obtained by the present technique combined with the standard addition method are compared with those by AAS with the D_2-lamp background correction in the other laboratory, and 33% at the most when the former results are compared with those by the calibration method. These agreements should be good enough for an inter-laboratory check. However, the precision is as poor as in the analysis of the Orchard Leaves. The precision in taking blood sample was found to be 17.8% in terms of r.s.d. In this case, the poor precision might be attributable mainly to the high viscosity of blood. In practice, the precision became poorer when the blood sample was rapidly sucked into the tip of the micropipette.

Table 1. Results of analysis

Element	Sample		Found* S.A.M.	Found* C.M.	Certificate or reference
Pb	NBS Orchard Leaves SRM 1571 (ppm)		45.3±0.9		45±3
	Human blood (n gml^{-1})	1	106±19	120±22	90†
		2	100±16	110±21	110†
		3	144±19	138±26	140†
	Volcanic ashes (ppm)	1		3.5±0.7‡	
		2		4.3±0.7§	
		3			5‖
Mn	Volcanic ashes (%)			0.069±0.007	0.07
Cr	Orchard Leaves (ppm)		(350°C)	2.4±0.5	2.6±0.3
			(700°C)	2.3±0.4	
	Volcanic ashes (ppm)	1		28±10‡	29‖
		2		34±5§	

* Results based on at least five replicate determinations.

† Taken from normal persons in December, 1979 and analysed in Public Health Research Laboratory, Medical School, Nagoya City University, Mizuhokawasumi, Mizuho-ku, Nagoya, Japan.

‡ Taken near the 8th station of Ontake Volcano in November, 1979.

§ Taken in Kaida Village, Nagano, Japan, in November, 1979.

‖ Taken in Shinbashi, Nagano, Japan, in November, 1979 and analysed in Nagano Research Institute for Health and Pollution, Kome-mura, Oaza-Amori, Nagano, Japan.

S.A.M. = Standard Addition Method.

C.M. = Calibration Method.

Precisions given in terms of S.D.

Temperatures in parentheses are charring temperature.

Another practical problem to be pointed out is the production of charcoal residue resulting from the pyrolysis. Figure 15 depicts the microphotograph of the internal space of the graphite tube atomizer which served 150 repeated measurements. Whiskers of charcoal are found bristling in the interior. In a series of measurements, the optical energy from the light source was screened off as the whiskers grew. Consequently, a newly prepared graphite tube atomizer served only less than 150 repeated atomizations in the blood analysis while it served more than 200 atomizations in the test analyses.

As for the volcanic ashes, a strict comparison cannot be made between the results obtained in the present and other works because of the differences in collecting time and location. It should be noted that the relative error amounts to 28% at the most in spite of the differences. Also in this case, the precision in taking the sample (12.6%) was dominant for the analytical precision. The residue problem was serious in this case. A silicate residue piled up in the interior of the graphite tube atomizer. This led to cutting off the source radiation after only 5–6 runs. Some technique such as air-blowing could be effective for removing the residue. To this end, a jet stream of air was

Fig. 15. Microphotograph of the internal space of the graphite tube atomizer which has served for 150 repeated atomizations of blood. Synthesized from three separate photographs.

introduced by inserting a tip (capillary tube) of the micropipette connected to an air compressor. By this means, the transmitted intensity was recovered.

The atomic Faraday effect has been applied to the trace determination of lead by atomic spectroscopy and in conjunction with the Zeeman effect the spectral features of the Faraday effect of lead have been discussed. Suspensions of solid samples (Orchard Leaves and volcanic ashes) and diluted human blood solutions have been analyzed after direct introduction into a graphite tube atomizer. Atomic Faraday spectroscopy reveals insensitivity to background scattering caused by non-atomic species generated in the atomizer but the problem of radiation loss by absorption by non-atomic species showed up. However, this can be overcome by a proposed correction method. Atomic Faraday spectroscopy coupled with this correction enabled us to perform rapid analyses by direct atomization with fairly accurate results. The precision turned out to be limited by the sampling with the micropipette and an additional problem became evident, namely that of residue build-up in the atomizer, which cuts off the source radiation after repeated runs.

1-7 Appendix

Calculation of a and B' for a single electron in hydrogen orbital [42, 43].

One of the origin of hfs, the Fermi interaction involves contacting of electron with the nucleus. The Hamiltonian required for the effect is given by the following equation:

$$H = -\frac{8\pi}{3} g_e \mu_e g_I \mu_N \delta(r) ,$$

where $\delta(r)$ is the Dirac delta function. The constant a is given as the eigenvalue:

$$a = -\frac{8\pi}{3} g_e \mu_e g_I \mu_N < \psi^* | \delta(r) | \psi > .$$

The integral term is the electron density at the nuclear position, $| \psi(0) |^2$. For a single s-electron, the integal is expressed as follows by substituting the Schrödinger wave function for ψ^* and ψ.

$$| \psi(0) |^2 = \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} \frac{4Z^3}{(n!)^2 n^5 a_1} e^{-2Z\sqrt{x^2+y^2+z^2}/na_1} L_n^1 \left(\frac{2Z\sqrt{x^2+y^2+z^2}}{na_1} \right) \delta(x)\delta(y)\delta(z)\, dxdydz ,$$

where Z is the effective nuclear charge, n the principal quantum number, a_1 the first Bohr radius and L_n^1 the Laguerre's associated polynominal.

Since $\int_{-\infty}^{\infty} f(x)\,\delta(x-\beta)dx = f(\beta)$,

$$\psi(0)^2 = \frac{4Z^3}{(n!)^2 n^5 a_1^3} (L_n^1(0))^2$$

$$= \frac{4Z^3}{n^3 a_1^3} .$$

In the classical treatment, it was suggested that Z^3 should be replaced by $Z_I Z_O^2$, where Z_I the atomic number and Z_O the nuclear charge outside. Consequently, the Fermi constant is given by

$$a = \frac{8\pi}{3} \frac{\mu_e}{1838} g_e g_I \frac{4 Z_I Z_O^2}{n^2 a_1^3}$$

$$= 0.105 g_I Z_I Z_O^2 / n^3 \quad (cm^{-1}) .$$

For the non penetrating electrons, l couples with s to yield a resultant j. Therefore, the Schrödinger wave function should be replaced by the Dirac electron.

The wave functions for $j = l \pm \frac{1}{2}$ are given by the following equations.
For $j = l + \frac{1}{2}$,

$$\psi\psi^* = R^2\theta^2$$
$$R^2 = M_r^2(F_l^2 + G_l^2)$$
$$F_l^2 = (N-p-n_r)\ (\sigma-\sigma_2)^2\ /\ (N+p+n_r)$$
$$\sigma_1 = (N+l+1)\, r^{p-1}e^{-kr}{}_1F_1(-n_r,\ 2p+1,\ 2kr)$$
$$\sigma_2 = -n_r r^{p-1}e^{-kr}{}_1F_1(-n_r+1,\ 2p+1,\ 2kr)$$

$${}_1F_1\ (\eta, \beta, \rho) = \sum_{j=0}^{\infty} \frac{\eta(\eta+1)\ \ldots\ldots\ (\eta+j-1)}{\beta(\beta+1)\ \ldots\ldots\ (\beta+j-1)}\ \rho^j$$

which terminates for negative value of η when $i = \eta$.

$$n_r = n - |l-1|$$

$$p = \sqrt{(l+1)^2-\alpha'^2}$$

$$k = l/a'N$$

$$N = \sqrt{n_r^2+(l+1)+2pn_r}$$

$$a' = 1/a_1Z$$

$$\alpha' = \alpha Z$$

$$\alpha = e_o^2/\hbar c$$

Here, α is the fine structure constant and e_o is the charge on electron. The radial normalization factor M_r is given by

$$M_r^2 = \frac{(N+p+n_r)\ (2k)^{2p+1}\,\Gamma(2p+n_r+1)}{n_r!\,2N(\Gamma(2p+1))^2\ ((N+l+1)^2+n_r(n_r+2p))}\ .$$

The angular function is given by the following equation:

$$\Theta^2 = (P_{l+1}^u P_{l+1}^u{}^* + P_{l+1}^{u+1} P_{l+1}^{u+1}{}^*)M_\theta^2 = P_\theta^2 M_\theta^2\ ,$$

where P_l^u is the associated Legendre's function expressed by

$$P_l^u = (l-u)!\ \sin^l\theta\ (\frac{d}{d\cos\theta})^{l+u}\ \frac{(\cos^2\theta-1)}{2!\,l!}\ e^{iu\varphi}\ .$$

The angular normalization factor M_θ is given by

$$M_\theta^2 = 1/4\pi(l+u+1)!(l-u)!\ .$$

where $u = m_j - 1/2$. For $j = l - 1/2$, l should be replaced by $-(l + 1)$. The integral term $|\psi(0)|^2$ is expressed as follows:

$$|\psi(0)|^2 = M_\theta^2 M_r^2 \int_{-\infty}^{\infty}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} P_\theta^2 (F_l^2 + G_l^2)\,\delta(x)\,\delta(y)\,\delta(z)\,\mathrm{d}x\mathrm{d}y\mathrm{d}z \ .$$

This integral value is zero unless P_θ^2 includes a constant term. For the constant term of P_θ^2, the integral is reduced to

$$|\psi(0)|^2 = M_\theta^2 M_r^2 P_k^2 \{F_l^2(0) + G_l^2(0)\} \ ,$$

where P_k^2 is the constant value of P_θ^2.

$$\sigma_1(0) = (N+l+1)\,0^{p-1}$$

$$\sigma_2(0) = -n_r 0^{p-1}$$

Except $^2S_{1/2}$ and $^2P_{1/2}$ terms, p is not unity. Therefore, the integral is zero for the other terms. The $^2S_{1/2}$ term has been treated above by the Schrödinger wave function. For the term $^2P_{1/2}$,

$$|\psi(0)|^2 = \frac{1}{4\pi}\,(N-l-n_r)^2 M_r^2 \ .$$

The Hamiltonian for the dipole-dipole interaction is given by

$$\mathrm{H} = \frac{-g_J \mu_e g_I \mu_N}{r^2}\left(\boldsymbol{I}\cdot\boldsymbol{J} - \frac{3(\boldsymbol{I}\cdot\boldsymbol{r})\,(\boldsymbol{J}\cdot\boldsymbol{r})}{r^2}\right) .$$

This is developed as follows:

$$\mathrm{H} = -g_J \mu_e g_I \mu_N (A + B + C + D + E + F) \ ,$$

where

$$A = I_Z J_Z (1 - 3\cos^2\theta)/r^3$$

$$B = (I_Z J_Z - \boldsymbol{I}\cdot\boldsymbol{J})\,(1 - 3\cos^2\theta)/2r^3$$

$$C = -3(I_Z J_+ + J_Z I_+)\,(\cos\theta \sin e^{-i\varphi})\,/\,2r^3$$

$$D = C^*$$

$$E = -3(I_+ J_+ \sin\theta e^{-2i\varphi})\,/\,4r^3$$

$$F = E^* \ .$$

Here, $I_+ = I_x + iI_y$ and $J_+ = J_x + iJ_y$.

The terms C, D, E and F are so small compared with A and B that they are usually omitted. The summation of A and B yields

$$A+B = (\boldsymbol{I}\cdot\boldsymbol{J}-3I_Z J_Z)\ \frac{3\cos^2\theta-1}{2r^3}\ .$$

Therefore, B' is given by

$$B' = g_J \mu_e g_I \mu_N < \psi^* \mid \frac{3\cos^2\theta-1}{2r^3} \mid \psi > .$$

For s-electron, because θ^2 has a constant value θ_k^2, the integral is given by

$$< \psi^* \mid \frac{3\cos^3\theta-1}{2r^3} \mid \psi > = \Theta_k^2 \int_0^\infty \frac{R^2 r^2}{2r^3}\, dr \int_0^\pi (3\cos^2\theta-1)\sin\theta\, d\theta\ .$$

Since the second integral has zero value,
$B' = 0$ for s-electron.

For non-penetrating electron, we can obtain the integral value by replacing ψ by the Dirac electron function.

$$< \psi^* \mid \frac{3\cos^3\theta-1}{2r^3} \mid \psi > = \frac{1}{2}\int_0^\infty \frac{R^2 r^2}{r^3}\, dr \int_0^\pi (3\cos^2\theta-1)\theta^2 \sin\theta d\theta\ .$$

The first integral

$$\int_0^\infty \frac{R^2}{r}\, dr = M_r^2 \int_0^\infty \frac{F_l^2+G_l^2}{r}\, dr$$

$$\int_0^\infty \frac{F^2}{r}\, dr = \frac{N-p-n_r}{N+p+n_r}\int_0^\infty \frac{(\sigma_1-\sigma_2)^2}{r}\, dr$$

$$\int_0^\infty \frac{G^2}{r}\, dr = \int_0^\infty \frac{(\sigma_1+\sigma_2)^2}{r}\, dr$$

$$\int_0^\infty \frac{(\sigma_1\mp\sigma_2)^2}{r}\, dr = \int_0^\infty r^{2p-3} e^{-2kr}\{(N+l+1)\,{}_1F_1(-n_r,\ 2p+1,\ 2kr)$$

$$\pm\ n_r\,{}_1F_1(-n_r+1,\ 2p+1,\ 2kr)\}^2 dr$$

Substituting ρ and β for $2kr$ and $2p+1$, respectively, we get

$$\int_0^\infty \frac{(\sigma_1\mp\sigma_2)^2}{r}\, dr = \frac{1}{2k^{2p-1}}\int_0^\infty \rho^{2p-3} e^{-\rho}[(N+l+1)\ \pm n_r$$

$$+\ \sum_{i=1}^{n_r-1} \frac{(N+l+1)\ \{\ (-n_r)\ (1-n_r)\ \ldots\ (i-l-n_r)\ \pm\ n_r(1-n_r)\ \ldots\ (i-n_r)\ \}}{\beta(\beta+1)\ \ldots\ (\beta+i-1)i!}\ \rho^i\ .$$

$$+ (N+l+1) \frac{(-n_r)\ (1-n_r)\ \ldots\ (-1)}{\beta(\beta+1)\ \ldots\ (\beta+n_r-1)n_r!}\ \rho^n r\,]^2 d\rho\ .$$

Since $\int_0^\infty \rho^i e^{-\rho} d\rho = \Gamma(i)$, we obtain the following equations:

$$F_l^2 = \frac{N-p-n_r}{N+p+n_r}\ \frac{1}{2k^{2p-2}}\ [(N+l+1+n_r)^2\ \Gamma(2p-3) + \ldots$$

$$+ (N+l+1)^2 \left\{ \frac{(-n_r)\ (1-n_r)\ \ldots\ (-1)}{\beta(\beta+1)\ \ldots\ (\beta+n_r-1)n_r!} \right\}^2 \Gamma(2n_r+2p-3)]\ .$$

$$G_l^2 = \frac{1}{2k^{2p-2}}\ [(N+l+1-n_r)^2\ \Gamma(2p-3) + \ldots$$

$$+ (N+l+1)^2 \left\{ \frac{(-n_r)\ (1-n_r)\ \ldots\ (-1)}{\beta(\beta+1)\ \ldots\ (\beta+n_r-1)n_r!} \right\}^2 \Gamma(2n_r+2p-3)]\ .$$

Thus, we can calculate the value of the constant of the dipole-dipole interaction, B'.

Computer programmes for the Zeeman splitting calculation

```
//FORTRAN
C
C ZEEMAN SPLIT OF HYPERFINE STRUCTURE
C PROGRAMMED BY K.KITAGAWA, 1976-12-18,327 GOSHITSU
C REVISED 1979-2-19
C DATA NO MAINI CR//RUN O IRERU,2 KAIME WA NASHI
C OUTPUT WA TAPE NIMO DETE DISPLAY NI TSUKAU
C
      COMMON A(10,10),N,C
      DIMENSION ZAMJ(10),ZAMI(10),EE(10),ZA(10),GJ(2)
      DIMENSION S(2),AL(2),AJ(2),AI(2),FERM(2),DIPL(2)
 1000 WRITE(6,2111)
 2111 FORMAT(1H1,'ZEEMAN SPLIT CAL.NO2 BY  K.KITAGAWA***SET DATA')
      PAUSE DATA
C HMIN,HMAX,HKIZ WA JIBA NO HANI TO KIZAMI
C JJLS WA COUPLING INDEX, JJLS=0 OR 1(L-S),2(J-J)
C HANI,DIV  WA TRIALS AND ERRORS CAL. NO HANIKIZAMI LIMIT
C RATE WA HANI NO KAKUDAI KIJUN((EX. HANI=0.2-1.0, DIV=500-1000
C RATE=0.6)
C S,L,J,I,FERMI,DIPOLE EFFECT O LOWER-UPPER NO JUN DE IRERU
C FORMAT WA HMAX,HKIZ,HANI,DIV-F11.4,JJLS-I4,S,L,J,I,-F11.4,FER,DPL-E10.3
C GI GA WAKARANAI TO KIWA GI=0.((F11.4)
C
C
      READ(5,1) HMIN,HMAX,HKIZ,HANI,DIV,RATE,GI
      READ(5,17) JJLS
      DO 1990 K=1,2
      READ(5,1) S(K),AL(K),AJ(K),AI(K),FERM(K),DIPL(K)
    1 FORMAT(4F11.4,3E10.3)
      IF(JJLS-1) 9210,9210,9211
 9210 LLLL=-11294
      WRITE(6,2600) LLLL
 2600 FORMAT(1H0,A2,"-COUPLING")
      IF(AJ(K)) 1928,1930,1928
 1930 GJ(K)=0.
      GO TO 9998
 1928 GJ(K)=AJ(K)*(AJ(K)+1.)+S(K)*(S(K)+1.)-AL(K)*(AL(K)+1.)
      GJ(K)=GJ(K)/(2.*AJ(K)*(AJ(K)+1.))+1.
      GO TO 9998
 9211 LLLL=-11823
      WRITE(6,2600) LLLL
```

```
      READ(5,1) GJ(K)
 9998 IF(K-1) 1650,1650,1651
 1650 WRITE(6,2877)
 2877 FORMAT(1H0,'QUANTUM NUMBERS OF THE LOWER STATE')
      GO TO 3888
 1651 WRITE(6,2888)
 2888 FORMAT(1H0,'QUANTUM NUMBERS OF THE UPPER STATE')
 3888 WRITE(6,5) S(K),AL(K),AJ(K),AI(K)
    5 FORMAT(1H0,'  S=',F4.1,'  L=',F4.1,'  J=',F4.1,'  I=',F4.1)
      WRITE(6,6) GJ(K),FERM(K),DIPL(K)
    6 FORMAT(1H ,'  GJ=',F7.4,'  FERMI FAC=',F7.4,'  DIPOLE FAC=',F7.4)
 1990 CONTINUE
      WRITE(7,77) (S(K),AL(K),AJ(K),AI(K),K=1,2)
   77 FORMAT(8F9.5)
      WRITE(7,77) HMIN,HMAX,HKIZ
      WRITE(7,77) (FERM(I),DIPL(I),I=1,2)
      RANG=HANI
      KCHK=1
      AMAG=4.6767E-02
      IF(AI(1)) 32,33,32
   32 WRITE(6,9274)
 9274 FORMAT(1H0,'INTERMIDIATE SPLIT-PURE ZEEMAN AND BACK GOUDSMIT')
      H=-HKIZ+HMIN
 2000 H=H+HKIZ
      IF(KCHK) 5525,5525,5526
 5525 RANG=RANG+HANI
 5526 IDIV=DIV+0.01
      KCHK=1
      WRITE(6,7) H
    7 FORMAT(1H0,//' MAGNETIC FIELD=',F8.3,' KG')
      DO 914 K=1,2
      IF(K-1) 25,25,24
   25 WRITE(6,325)
  325 FORMAT(1H0,/' ENERGY LEVELS OF THE LOWER STATE')
      GO TO 369
   24 WRITE(6,324)
  324 FORMAT(1H0,/' ENERGY LEVELS OF THE UPPER STATE')
  369 AMAX=AI(K)+AJ(K)
      MMAF=2.*AMAX+1.01
      NAXI=2.*AI(K)+1.01
      NAXJ=2.*AJ(K)+1.01
      DO 914 NF=1,MMAF
      AMMF=AMAX-FLOAT(NF)+1.
      WRITE(6,20) AMMF
   20 FORMAT(1H ,'MF=',F6.2/)
      NSS=0
      DO 900 IE=1,IDIV
      E=-RANG+2.*RANG*FLOAT(IE)/FLOAT(IDIV)
      N=0
      DO 920 NI=1,NAXI
      AMI=AI(K)-FLOAT(NI)+1.
      DO 920 NJ=1,NAXJ
      AMJ=AJ(K)-FLOAT(NJ)+1.
      IF(AMI+AMJ-AMMF) 920,200,920
  200 IF(ABS(AMMF)-AMAX) 300,950,300
  300 N=N+1
      A(N,N)=(GJ(K)*AMJ-AMI*GI/1836.1)*AMAG*H
      A(N,N)=A(N,N)+AMI*AMJ*(FERM(K)-2.*DIPL(K))-E
      ZA(N)=A(N,N)+E
      ZAMJ(N)=AMJ
      ZAMI(N)=AMI
      AAA=SQRT((AJ(K)-AMJ)*(AJ(K)+AMJ+1.)*(AI(K)+AMI)*(AI(K)-AMI+1.))
      AAA=0.5*AAA
      A(N,N+1)=AAA*(FERM(K)+DIPL(K))
      IF(N-1) 920,920,927
  927 AAB=SQRT((AJ(K)+AMJ)*(AJ(K)-AMJ+1.)*(AI(K)-AMI)*(AI(K)+AMI+1.))
      AAB=0.5*AAB
      A(N,N-1)=AAB*(FERM(K)+DIPL(K))
  920 CONTINUE
      DO 59 KN=1,N
      DO 59 JN=1,N
      IF(KN-JN) 60,59,60
```

```
   60 IF(IABS(KN-JN)-1) 70,59,70
   70 A(KN,JN)=0.
   59 CONTINUE
      CALL DETM
      IF(IE-1) 909,909,600
  600 HAND=CO*C
      IF(HAND) 800,800,909
  800 WRITE(6,69) E
   69 FORMAT(1H+,4X,E12.4,2X)
      IF(ABS(E)-RATE*RANG) 274,1955,1955
 1955 KCHK=0
  274 NSS=NSS+1
      EE(NSS)=E
  909 CO=C
  900 CONTINUE
      WRITE(6,19)
   19 FORMAT(1H ,2X)
      WRITE(7,17) NSS
   17 FORMAT(I4)
      DO 261 NNSS=1,NSS
      DO 262 NNN=1,N
      Z=ABS(ZA(NNN)-EE(NNSS))
      IF(NNN-1) 4001,4001,3002
 3002 IF(ZZMI-Z) 262,262,4001
 4001 ZZMI=Z
      NNNO=NNN
  262 CONTINUE
      WRITE(6,99) ZAMJ(NNNO),ZAMI(NNNO)
      IF(H-HMAX-HKIZ+1.0E-03) 84,85,85
   85 WRITE(7,77) ZAMJ(NNNO),ZAMI(NNNO)
   84 WRITE(7,1976) EE(NNSS)
 1976 FORMAT(E12.4)
  261 CONTINUE
      GO TO 914
  950 EO=(GJ(K)*AMJ-AMI*GI/1836.1)*AMAG*H+AMI*AMJ*(FERM(K)-2.*DIPL(K))
      WRITE(6,99) AMJ,AMI,EO
   99 FORMAT(1H+,' MJ=',F4.1,' MI=',F4.1,2X,E12.4)
      NSK=1
      IF(H-HMAX-HKIZ+1.0E-03) 181,182,182
  181 WRITE(7,17) NSK
      WRITE(7,1976) EO
      GO TO 914
  182 IF(K-1) 183,183,186
  183 IF(NF-1) 185,185,186
  185 WRITE(7,1765)
 1765 FORMAT(1H+,80X)
  186 WRITE(7,17) NSK
      WRITE(7,77) AMJ,AMI
      WRITE(7,1976) EO
  914 CONTINUE
      IF(H+1.0E-03-HMAX-HKIZ) 2000,1000,1000
   33 WRITE(6,1111)
 1111 FORMAT(1H0,'PURE ZEEMAN SPLIT')
      H=-HKIZ+HMIN
   15 H=H+HKIZ
      WRITE(6,7) H
      DO 790 JJJ=1,2
      IF(JJJ-1) 969,969,968
  969 WRITE(6,325)
      GO TO 967
  968 WRITE(6,324)
  967 IAXX=2.*AJ(JJJ)+1.01
      WRITE(7,17) IAXX
      DO 790 IXX=1,IAXX
      XX=AJ(JJJ)-FLOAT(IXX)+1.
      EXX=GJ(JJJ)*XX*AMAG*H
      WRITE(6,13) XX,EXX
   13 FORMAT(1H ,'MJ=',F7.3,3X,E12.4)
      WRITE(7,77) XX
      WRITE(7,1976) EXX
  790 CONTINUE
      IF(H-HMAX) 15,1000,1000
      STOP
      END
```

```
C
C GYØRETSUSHIKI NØ KEISAN--- 10 GEN MADE
C
C
      SUBRØUTINE DETM
      CØMMØN A(10,10),N,C
      DIMENSIØN B(10)
      JJ=0
      DØ 10 K=1,N
      BIG=ABS(A(K,K))
      IP=K
      K1=K+1
      IF(K1-N) 12,12,14
   12 DØ 13 I=K1,N
      IF(ABS(A(I,K))-BIG) 13,13,15
   15 BIG=ABS(A(I,K))
      IP=I
   13 CØNTINUE
   14 IF(BIG-1.0E-30) 55,17,17
   17 IF(IP-K) 18,19,18
   18 DØ 25 J=1,N
      TEMP=A(K,J)
      A(K,J)=A(IP,J)
      A(IP,J)=TEMP
   25 CØNTINUE
      JJ=JJ+1
   19 B(K)=A(K,K)
      DØ 20 J=K,N
      A(K,J)=A(K,J)/B(K)
   20 CØNTINUE
      DØ 10 I=1,N
      IF(I-K) 31,10,31
   31 W=A(I,K)
      DØ 30 J=K,N
      A(I,J)=A(I,J)-W*A(K,J)
   30 CØNTINUE
   10 CØNTINUE
      C=1.
      DØ 50 I=1,N
      C=C*B(I)
   50 CØNTINUE
      C=C*(-1.)**JJ
      GØ TØ 56
   55 C=1.0E-60
   56 RETURN
      END
```

```
)J ØUTPUT END
```

```
//FØRTRAN
C     INDX=0  LØWER LEVEL,  INDX=1 UPPER LEVEL,  INDX=2  SHIGUMA AND PAI
C     GAN1 WA KAKUDAI NØ PARAMETER,AI WA KAKUSPIN
C     IND2=0 SHIGUMA PAI,  IND2=1 SHIGUMA DAKE
      CØMMØN II,IJK,IL,IH,II1(30),ZJL1(30),ZIL1(30),ZJH1(30),ZIH1(30)
      CØMMØN MJL(50),MIL(50),MJH(50),MIH(50)
      DIMENSIØN IA(101),MM2(2),S(2),AL(2),AJ(2),AI(2),FERM(2),DIPL(2)
      DIMENSIØN E(100)
      READ(5,100) INDX,IND2,GAN1,AI(1)
      PAUSE DATO
      IF(AI(1)) 107,901,107
  107 IN1=0
  908 IN0=0
```

```
      IN1=IN1+1
      M2=0
  902 IN0=IN0+1
      READ(5,100) NSS
      M1=M2+1
      M2=M1+NSS-1
      DØ 930 K=M1,M2
      READ(5,104) AMJ,AMI
      READ(5,102) ENG
      IF(IN1-1) 914,913,914
  913 MJL(K)=2.*AMJ
      MIL(K)=2.*AMI
      E(K+50)=ENG
      GØ TØ 930
  914 MJH(K)=2.*AMJ
      MIH(K)=2.*AMI
      E(K)=ENG
  930 CØNTINUE
      IF(IN0-1) 903,902,903
  903 IF(NSS-1) 902,909,902
  909 MM2(IN1)=M2
      IF(IN1-1) 901,908,901
  901 PAUSE DAT1
      READ(5,104) (S(K),AL(K),AJ(K),AI(K),K=1,2)
      READ(5,104) HMIN,HMAX,DIVS
      H=HMAX-HMIN
      READ(5,104) (FERM(I),DIPL(I),I=1,2)
      DØ 500 K=1,2
      IF(K-1) 300,300,301
  300 WRITE(6,201)
      GØ TØ 302
  301 WRITE(6,202)
  302 WRITE(6,203) S(K),AL(K),AJ(K),AI(K)
  500 CØNTINUE
      WRITE(6,207) (FERM(I),DIPL(I),I=1,2)
      WRITE(6,204) HMIN,HMAX
      WRITE(6,205) DIVS
      SCAL=1./GAN1
      WRITE(6,206) SCAL,INDX
      IHI=5.*H+1.1
      IDIV=5.*DIVS+0.01
      J=0
      IF(AI(1)) 51,52,51
   52 IJ=0
   53 IJ=IJ+1
      READ(5,100) J21
      DØ 33 K=1,J21
      READ(5,104) AAMJ
      READ(5,102) ENG
      IF(IJ-1) 54,55,54
   55 MJL(K)=2.*AAMJ
      MIL(K)=0
      E(K+50)=ENG
      GØ TØ 33
   54 MJH(K)=2.*AAMJ
      MIH(K)=0
      E(K)=ENG
   33 CONTINUE
      MM2(IJ)=J21
      IF(IJ-2) 53,1,53
   51 IN1=0
    8 IN0=0
      IN1=IN1+1
      M2=0
    2 IN0=IN0+1
      READ(5,100) NSS
      M1=M2+1
      M2=M1+NSS-1
      DØ 30 K=M1,M2
      READ(5,102) ENG
      IF(IN1-1) 14,13,14
   13 E(K+50)=ENG
```

```
      GØ TØ 30
   14 E(K)=ENG
   30 CØNTINUE
      IF(INO-1) 3,2,3
    3 IF(NSS-1) 2,9,2
    9 MM2(IN1)=M2
      IF(IN1-1) 1,8,1
    1 J=J+1
      DØ 31 I=1,101
   31 IA(I)=16448
      IA(1)=-14016
      IA(51)=-14016
      IA(101)=-14016
      IF(J-1) 21,20,21
   21 IF(J-IHI) 22,20,22
   20 DØ 32 I=1,101
   32 IA(I)=24640
   22 JJ=(J-1)/IDIV
      IF(JJ*IDIV+1-J) 26,25,26
   25 IF(AI(1)) 60,61,60
   61 IF(INDX-1) 62,63,65
   62 N1=51
      N2=MM2(1)+50
      GØ TØ 29
   63 N1=1
      N2=MM2(2)
      GØ TØ 29
   60 IF(INDX-1) 16,15,65
   16 N1=51
      N2=MM2(1)+50
      GØ TØ 29
   15 N1=1
      N2=MM2(2)
   29 DØ 12 I=N1,N2
      IF(E(I)) 23,24,24
   24 II=E(I)*50.*GAN1+51.5
      IF(II-101) 28,28,12
   28 IA(II)=23616
      GØ TØ 12
   23 II=E(I)*50.*GAN1+50.5
      IF(II) 12,12,27
   27 IA(II)=23616
   12 CØNTINUE
      GØ TØ 26
   65 NN1=MM2(1)
      NN2=MM2(2)
      IJK=0
      DØ 70 IL=1,NN1
      DØ 71 IH=1,NN2
      EDEL=E(IH)-E(IL+50)
      IF(EDEL) 81,80,80
   80 II=EDEL*50.*GAN1+51.5
      IF(II-101) 90,90,71
   81 II=EDEL*50.*GAN1+50.5
      IF(II) 71,90,90
   90 IF(MIH(IH)-MIL(IL)) 71,91,71
   91 MJDE=MJH(IH)-MJL(IL)
      IF(IND2-1) 350,350,92
  350 IF(MJDE) 92,95,92
   92 IF(MJDE-2) 93,96,93
   93 IF(MJDE+2) 71,97,71
   95 IF(IA(II)-19268) 351,75,351
  351 IF(IA(II)-20032) 352,75,352
  352 IF(IA(II)-23616) 354,75,354
  354 IA(II)=32320
      GØ TØ 75
   96 IF(IA(II)-19268) 353,99,353
  353 IF(IA(II)-23616) 355,99,355
  355 IA(II)=20032
      GØ TØ 75
   97 IF(IA(II)-20032) 94,99,94
   94 IF(IA(II)-23616) 356,99,356
```

```
   99 IA(II)=23616
      GO TO 75
  356 IA(II)=19268
   75 CALL SUB1
   71 CONTINUE
   70 CONTINUE
   26 WRITE(6,200) (IA(II),II=1,101)
      IF(J-IHI) 7,5,5
    7 JJ=J/IDIV
      IF(JJ*IDIV-J) 1,50,1
   50 IN1=0
      IF(AI(1)) 8,52,8
  100 FORMAT(2I4,2F5.1)
  102 FORMAT(E12.4)
  104 FORMAT(8F9.5)
  200 FORMAT(1H ,101A1)
  201 FORMAT(1H ,'QUANTUM NUMBERS OF THE LOWER STATE')
  202 FORMAT(1H ,'QUANTUM NUMBERS OF THE UPPER STATE')
  203 FORMAT(1H+,'      S=',F4.1,'  L=',F4.1,'  J=',F4.1,'  I=',F4.1)
  204 FORMAT(1H ,'MAGNETIC FIELD ',F5.1,' KG TO',F5.1,'KG')
  205 FORMAT(1H ,'ABSCISSA DIVISION=',F5.1,' KG')
  206 FORMAT(1H ,'FULL SCALE=+-',F4.1,' /CM',7X,'0=L,1=H,2=T**',I2///)
  207 FORMAT(1H ,'  F1=',F9.5,'  D1=',F9.5,'  F2=',F9.5,'  D2=',F9.5)
    5 WRITE(6,208)
      WRITE(6,209)(II1(JK),ZJL1(JK),ZIL1(JK),ZJH1(JK),ZIH1(JK),JK=1,IJK)
  208 FORMAT(///' ','COLUMN',8X,'JL',8X,'IL',11X,'JU',8X,'IU')
  209 FORMAT(1H ,I4,2X,2F10.1,3X,2F10.1)
      STOP
      END



C
      SUBROUTINE SUB1
      COMMON II,IJK,IL,IH,II1(30),ZJL1(30),ZIL1(30),ZJH1(30),ZIH1(30)
      COMMON MJL(50),MIL(50),MJH(50),MIH(50)
      IJK=IJK+1
      II1(IJK)=II
      ZJL1(IJK)=FLOAT(MJL(IL))/2.
      ZJH1(IJK)=FLOAT(MJH(IH))/2.
      ZIL1(IJK)=FLOAT(MIL(IL))/2.
      ZIH1(IJK)=FLOAT(MIH(IH))/2.
      RETURN
      END



)J OUTPUT END



READY
    //FORTRAN
      COMMON NKJ,AKJ
      DIMENSION X(20,2),XX(40),THET(4,4),YX(20,1)
   94 WRITE(6,2)
    2 FORMAT(1H1,'CAL. OF D-D INTERACTION**SET**DATA**')
      PAUSE DATA
      READ(5,10) N,L,AL,AS,AJ,GI,ZI,Z0
   10 FORMAT(2I3,6F10.5)
      GJ=AJ*(AJ+1.)+(AS+1.)*AS-AL*(AL+1.)
      GJ=GJ/(2.*AJ*(AJ+1.))+1.
      WRITE(6,877) N,L,AL,AS,AJ,GI,ZI,Z0,GJ
  877 FORMAT(1H0,'FACTORS*N,L,AL,AS,AJ,GI,ZI,Z0,GJ=',2I5,7F10.5)
      Z=(ZI*Z0**2)**(1./3.)
```

```
      WRITE(6,1)Z
    1 FØRMAT(1H0,'EFFECTIVE NUCLEAR CHARGE Z=',F10.5)
      THET(1,1)=0.
      THET(2,1)=6.366662E-02
      THET(2,2)=-6.366662E-02
      THET(3,1)=-4.45473E-02
      THET(3,2)=2.38732E-01
      THET(3,3)=1.23413E-01
      THET(4,1)=-5.30516E-02
      THET(4,2)=-7.5787E-03
      THET(4,3)=4.54728E-02
      THET(4,4)=7.4367E-02
      NHAN=2.*(AJ-FLØAT(L))+1.0E-04
      MHAN=IABS(NHAN)-1
      IF(MHAN) 40,41,40
   40 WRITE(6,1040)
 1040 FØRMAT(1H1,' NØT TREATED------SET AGAIN PLEASE--------')
      GØ TØ 94
   41 IF(NHAN) 42,40,43
   42 LL=(-1)*(L+1)
      NTHT=L
      GØ TØ 44
   43 LL=L
      NTHT=L+1
   44 NR=N-IABS(LL-1)
      ALP=5.3E-05*Z**2
      NP=IABS(LL+1)
      ANN=SQRT(FLØAT(NR)**2+FLØAT(LL+1)**2+2.*FLØAT(NP*NR))
      A1=0.528E-08
      AZ=A1/Z
      AK=1./AZ/ANN
      Q=2*NP+1
      WRITE(6,1984)NR,NP,ANN,AZ,AK,Q
 1984 FØRMAT(1H0,'NR,NP,ANN,AZ,AK,Q=',2I3,4E15.5)
      DØ 101 I12=1,2
      IF(I12-1) 1985,1985,1986
 1985 WRITE(6,1987)I12
 1987 FØRMAT(1H0,'FACTØRS ØF SIGMA',I2)
      GØ TØ 1989
 1986 WRITE(6,1987)I12
 1989 QQ=Q
      PCC=1
      NX=2
      X(1,I12)=1.
      WRITE(6,1800)X(1,I12),I12
 1800 FØRMAT(1H0,E20.5,'*X',I2,' **  0')
      IF(I12-1) 31,31,30
   31 NRR=(-1)*NR
      GØ TØ 32
   30 NRR=(-1)*NR+1
   32 NKJ=NX-1
      CALL KAIJ
      CC=PCC*FLØAT(NRR)/QQ
      NXX=NX-1
      X(NX,I12)=CC/AKJ
      WRITE(6,1801)X(NX,I12),I12,NXX
 1801 FØRMAT(1H ,E20.5,'*X',I2,' **',I3)
      NRR=NRR+1
      IF(NRR) 34,35,35
   34 QQ=QQ+1.
      NX=NX+1
      PCC=CC
      GØ TØ 32
   35 IF(I12-1) 36,36,37
   36 NXM1=NX
  101 CØNTINUE
   37 NXM2=NX
      DØ 100 IFG=1,2
      IF(IFG-1) 38,38,39
   38 SSS=-1.
      WRITE(6,1991)
 1991 FØRMAT(1H0,'FACTØRS ØF FL AND FL**2')
      GØ TØ 50
```

```
   39 SSS=1.
      WRITE(6,1992)
 1992 FORMAT(1HO,'FACTORS OF GL AND GL**2')
   50 DO 721 NX=1,NXM2
      YX(NX,1)=X(NX,1)*(ANN+FLOAT(LL)+1.)
      YX(NX,1)=YX(NX,1)+X(NX,2)*SSS*(-1.)*FLOAT(NR)
      NXY=NX-1
      WRITE(6,2003)YX(NX,1),NXY
  721 CONTINUE
      YX(NXM1,1)=X(NXM1,1)*(ANN+FLOAT(LL)+1.)
      NXMD=NXM1-1
      WRITE(6,2003)YX(NXM1,1),NXMD
      NX2S=2*(NXM1-1)+1
      DO 801 NX=1,NX2S
  801 XX(NX)=0.
      DO 722 NX=1,NX2S
      DO 723 NX1=1,NX2S
      DO 724 NX2=1,NX2S
      NHN=NX1+NX2-1
      IF(NHN-NX) 724,1722,724
 1722 NKJ=2*NP-3+NHN-1
      CALL KAIJ
      XX(NX)=XX(NX)+YX(NX1,1)*YX(NX2,1)*AKJ
  724 CONTINUE
  723 CONTINUE
  722 CONTINUE
      FL2=0.
      GL2=0.
      DO 725 NX=1,NX2S
      NXX=NX-1
      WRITE(6,2003)XX(NX),NXX
 2003 FORMAT(1H ,E20.5,'(',I3,')')
      IF(IFG-1) 52,52,51
   52 FL2=FL2+(ANN-FLOAT(NP+NR))*XX(NX)/(ANN+FLOAT(NP+NR))
      GO TO 725
   51 GL2=GL2+XX(NX)
  725 CONTINUE
  100 CONTINUE
      WRITE(6,2004) FL2,GL2
 2004 FORMAT(1HO,'FFL**2=',E15.5,8X,'GGL**2=',E15.5)
      FC=1./(2.*AK)**(2.*FLOAT(NP)-2.)
      FL2=FL2*FC
      GL2=GL2*FC
      WRITE(6,2005)FL2,GL2
 2005 FORMAT(1HO,'FL**2= ',E15.5,8X,'GL**2=',E15.5)
      NKJ=2*NP+NR+1
      CALL KAIJ
      C1=AKJ
      NKJ=2*NP+1
      CALL KAIJ
      C2=AKJ**2
      NKJ=NR
      CALL KAIJ
      C3=AKJ
      C4=ANN+FLOAT(NP+NR)
      C5=(2.*AK)**(2*NP+1)
      C6=(ANN+FLOAT(LL+1))**2+FLOAT(NR*(NR+2*NP))
      AMR2=(C4*C5*C1)/(C3*2.*ANN*C2*C6)
      WRITE(6,2006)AMR2,C1,C2,C3,C4,C5,C6
 2006 FORMAT(1HO,'R-NORMALIZATION FAC.,MR**2=',7E11.4)
      R2=AMR2*(FL2+GL2)
      WRITE(6,2007)R2
 2007 FORMAT(1HO,'R-INTEGRAL VALUE,RR=',E15.5)
      DO 730 JJJ=1,NTHT
      AINT=R2*THET(NTHT,JJJ)/2.
      JJS=2*(JJJ-1)+1
      WRITE(6,2008)JJS,AINT
 2008 FORMAT(1HO,'INTEGRAL VALUE(/MJ/=',I3,'/2  )=',E20.5)
      WRITE(6,2009)THET(NTHT,JJJ)
 2009 FORMAT(1H+,'  (THETA-INTEGRAL VALUE=',E15.5,')')
      AMU2=(-1.)*(9.174E-21)**2/1838.
      CONS=AMU2*GJ*GI*AINT
      BBBB=CONS*5.03446E15
```

```
  730 WRITE(6,2010)BBBB
 2010 FØRMAT(1HØ,'D-D INTERACTIØN CØNST. B=',E16.5,' /CM')
      GØ TØ 94
      STØP
      END



C
C
C
C
C KAIJØ NØ KEISAN
C
C
C
      SUBRØUTINE KAIJ
      CØMMØN NKJ,AKJ
      AKJ=1.
      IF(NKJ) 100,100,200
  200 DØ 19 I=1,NKJ
      ANK=I
   19 AKJ=AKJ*ANK
  100 RETURN
      END


ØBJ ØUTPUT END


//FØRTRAN
C
C ZEEMAN SPLIT ØF HYPERFINE STRUCTURE FØR I IS NØT ZERØ
C PRØGRAMMED BY K.KITAGAWA, 1976-12-18,327 GØSHITSU
C REVISED 1979-2-19, 1980-10-8(INCLUDING QUADRØPØLE INTERACTIØN)
C DATA NØ MAENI CR//RUN Ø IRERU,2 KAIME WA NASHI
C ØUTPUT WA TAPE NIMØ DETE DISPLAY NI TSUKAU
C
      CØMMØN A(10,10),N,C
      DIMENSIØN ZAMJ(10),ZAMI(10),EE(10),ZA(10),GJ(2)
      DIMENSIØN S(2),AL(2),AJ(2),AI(2),FERM(2),DIPL(2),BQP(2)
 1000 WRITE(6,2111)
 2111 FØRMAT(1H1,'ZEEMAN SPLIT CAL.NØ2 BY  K.KITAGAWA***SET DATA')
      PAUSE DATA
C HMIN,HMAX,HKIZ WA JIBA NØ HANI TØ KIZAMI
C JJLS WA CØUPLING INDEX, JJLS=0 ØR 1(L-S),2(J-J)
C HANI,DIV  WA TRIALS AND ERRØRS CAL. NØ HANIKIZAMI LIMIT
C RATE WA HANI NØ KAKUDAI KIJUN((EX. HANI=0.2-1.0, DIV=500-1000
C RATE=0.6)
C S,L,J,I,FERMI,DIPØLE EFFECT Ø LØWER-UPPER NØ JUN DE IRERU
C FØRMAT WA HMAX,HKIZ,HANI,DIV-F11.4,JJLS-I4,S,L,J,I,-F11.4,FER,DPL-E10.
C GI GA WAKARANAI TØ KIWA GI=0.((F11.4)                                3
C
C    BQP=QUADRØPØLE INTERACTIØN FACTØR
C
      READ(5,1) HMIN,HMAX,HKIZ,HANI,DIV,RATE,GI
      READ(5,17) JJLS
      DØ 1990 K=1,2
      READ(5,1) S(K),AL(K),AJ(K),AI(K),FERM(K),DIPL(K),BQP(K)
    1 FØRMAT(4F11.4,4E10.3)
      IF(JJLS-1) 9210,9210,9211
 9210 LLLL=-11294
      WRITE(6,2600) LLLL
```

```
2600 FORMAT(1H0,A2,'-COUPLING')
     IF(AJ(K)) 1928,1930,1928
1930 GJ(K)=0.
     GO TO 9998
1928 GJ(K)=AJ(K)*(AJ(K)+1.)+S(K)*(S(K)+1.)-AL(K)*(AL(K)+1.)
     GJ(K)=GJ(K)/(2.*AJ(K)*(AJ(K)+1.))+1.
     GO TO 9998
9211 LLLL=-11823
     WRITE(6,2600) LLLL
     READ(5,1) GJ(K)
9998 IF(K-1) 1650,1650,1651
1650 WRITE(6,2877)
2877 FORMAT(1H0,'QUANTUM NUMBERS OF THE LOWER STATE')
     GO TO 3888
1651 WRITE(6,2888)
2888 FORMAT(1H0,'QUANTUM NUMBERS OF THE UPPER STATE')
3888 WRITE(6,5) S(K),AL(K),AJ(K),AI(K)
   5 FORMAT(1H0,'  S=',F4.1,'  L=',F4.1,'  J=',F4.1,'  I=',F4.1)
     WRITE(6,6) GJ(K),FERM(K),DIPL(K)
   6 FORMAT(1H ,'  GJ=',F7.4,'  FERMI FAC=',F7.4,'  DIPOLE FAC=',F7.4)
1990 CONTINUE
     WRITE(7,77) (S(K),AL(K),AJ(K),AI(K),K=1,2)
  77 FORMAT(8F9.5)
     WRITE(7,77) HMIN,HMAX,HKIZ
     WRITE(7,77) (FERM(I),DIPL(I),I=1,2)
     RANG=HANI
     KCHK=1
     AMAG=4.6767E-02
     IF(AI(1)) 32,33,32
  32 WRITE(6,9274)
9274 FORMAT(1H0,'INTERMIDIATE SPLIT-PURE ZEEMAN AND BACK GOUDSMIT')
     H=-HKIZ+HMIN
2000 H=H+HKIZ
     IF(KCHK) 5525,5525,5526
5525 RANG=RANG+HANI
5526 IDIV=DIV+0.01
     KCHK=1
     WRITE(6,7) H
   7 FORMAT(1H0,//' MAGNETIC FIELD=',F8.3,' KG')
     DO 914 K=1,2
     IF(K-1) 25,25,24
  25 WRITE(6,325)
 325 FORMAT(1H0,/' ENERGY LEVELS OF THE LOWER STATE')
     GO TO 369
  24 WRITE(6,324)
 324 FORMAT(1H0,/' ENERGY LEVELS OF THE UPPER STATE')
 369 AMAX=AI(K)+AJ(K)
     MMAF=2.*AMAX+1.01
     NAXI=2.*AI(K)+1.01
     NAXJ=2.*AJ(K)+1.01
     DO 914 NF=1,MMAF
     AMMF=AMAX-FLOAT(NF)+1.
     WRITE(6,20) AMMF
  20 FORMAT(1H ,'MF=',F6.2/)
     NSS=0
     DO 900 IE=1,IDIV
     E=-RANG+2.*RANG*FLOAT(IE)/FLOAT(IDIV)
     N=0
     DO 920 NI=1,NAXI
     AMI=AI(K)-FLOAT(NI)+1.
     DO 920 NJ=1,NAXJ
     AMJ=AJ(K)-FLOAT(NJ)+1.
     IF(AMI+AMJ-AMMF) 920,200,920
 200 IF(ABS(AMMF)-AMAX) 300,950,300
 300 N=N+1
     FQ=BQP(K)/(2.*AI(K)*AJ(K)*(2.*AI(K)-1.)*(2.*AJ(K)-1.))
     Y1=AI(K)+AMI
     Y2=AI(K)-AMI
     Y3=AJ(K)+AMJ
     Y4=AJ(K)-AMJ
     FQNM=FQ*1.5*SQRT((Y1+1.)*Y2*(Y4+1.)*Y3)
     FQNN=FQ*1.5*SQRT((Y2+1.)*Y1*(Y3+1.)*Y4)
```

```
      QPT=(Y1*(Y2+1.)+Y2*(Y1+1.))*(Y3*(Y4+1.)+Y4*(Y3+1.))
      QPT=QPT-(Y2*(Y1+1.)-Y1*(Y2+1.))*(Y4*(Y3+1.)-Y3*(Y4+1.))
      QPT=((QPT/8.)*3.+AMI*AMJ*(3.*AMI*AMJ+1.5))*FQ
      A(N,N)=(GJ(K)*AMJ-AMI*GI/1836.1)*AMAG*H
      A(N,N)=A(N,N)+AMI*AMJ*(FERM(K)-2.*DIPL(K))+QPT-E
      ZA(N)=A(N,N)+E
      ZAMJ(N)=AMJ
      ZAMI(N)=AMI
      AAA=SQRT((AJ(K)-AMJ)*(AJ(K)+AMJ+1.)*(AI(K)+AMI)*(AI(K)-AMI+1.))
      AAA=0.5*AAA
      A(N,N+1)=AAA*(FERM(K)+DIPL(K))+FQNN
      IF(N-1) 920,920,927
  927 AAB=SQRT((AJ(K)+AMJ)*(AJ(K)-AMJ+1.)*(AI(K)-AMI)*(AI(K)+AMI+1.))
      AAB=0.5*AAB
      A(N,N-1)=AAB*(FERM(K)+DIPL(K))+FQNM
  920 CØNTINUE
      DØ 59 KN=1,N
      DØ 59 JN=1,N
      IF(KN-JN) 60,59,60
   60 IF(IABS(KN-JN)-1) 70,59,70
   70 A(KN,JN)=0.
   59 CØNTINUE
      CALL DETM
      IF(IE-1) 909,909,600
  600 HANB=CØ*C
      IF(HANB) 800,800,909
  800 WRITE(6,69) E
   69 FØRMAT(1H+,4X,E12.4,2X)
      IF(ABS(E)-RATE*RANG) 274,1955,1955
 1955 KCHK=0
  274 NSS=NSS+1
      EE(NSS)=E
  909 CØ=C
  900 CØNTINUE
      WRITE(6,19)
   19 FØRMAT(1H ,2X)
      WRITE(7,17) NSS
   17 FØRMAT(I4)
      DØ 261 NNSS=1,NSS
      DØ 262 NNN=1,N
      Z=ABS(ZA(NNN)-EE(NNSS))
      IF(NNN-1) 4001,4001,3002
 3002 IF(ZZMI-Z) 262,262,4001
 4001 ZZMI=Z
      NNNØ=NNN
  262 CØNTINUE
      WRITE(6,99) ZAMJ(NNNØ),ZAMI(NNNØ)
      IF(H-HMAX-HKIZ+1.0E-03) 84,85,85
   85 WRITE(7,77) ZAMJ(NNNØ),ZAMI(NNNØ)
   84 WRITE(7,1976) EE(NNSS)
 1976 FØRMAT(E12.4)
  261 CØNTINUE
      GØ TØ 914
  950 EØ=(GJ(K)*AMJ-AMI*GI/1836.1)*AMAG*H+AMI*AMJ*(FERM(K)-2.*DIPL(K))
      WRITE(6,99) AMJ,AMI,EØ
   99 FØRMAT(1H+,' MJ=',F4.1,' MI=',F4.1,2X,E12.4)
      NSK=1
      IF(H-HMAX-HKIZ+1.0E-03) 181,182,182
  181 WRITE(7,17) NSK
      WRITE(7,1976) EØ
      GØ TØ 914
  182 IF(K-1) 183,183,186
  183 IF(NF-1) 185,185,186
  185 WRITE(7,1765)
 1765 FØRMAT(1H+,80X)
  186 WRITE(7,17) NSK
      WRITE(7,77) AMJ,AMI
      WRITE(7,1976) EØ
  914 CØNTINUE
      IF(H+1.0E-03-HMAX-HKIZ) 2000,1000,1000
   33 STØP IEQ0
      END
```

```
C
C GYØRETSUSHIKI NØ KEISAN--- 10 GEN MADE
C
C
      SUBRØUTINE DETM
      CØMMØN A(10,10),N,C
      DIMENSIØN B(10)
      JJ=0
      DØ 10 K=1,N
      BIG=ABS(A(K,K))
      IP=K
      K1=K+1
      IF(K1-N) 12,12,14
   12 DØ 13 I=K1,N
      IF(ABS(A(I,K))-BIG) 13,13,15
   15 BIG=ABS(A(I,K))
      IP=I
   13 CØNTINUE
   14 IF(BIG-1.0E-30) 55,17,17
   17 IF(IP-K) 18,19,18
   18 DØ 25 J=1,N
      TEMP=A(K,J)
      A(K,J)=A(IP,J)
      A(IP,J)=TEMP
   25 CØNTINUE
      JJ=JJ+1
   19 B(K)=A(K,K)
      DØ 20 J=K,N
      A(K,J)=A(K,J)/B(K)
   20 CØNTINUE
      DØ 10 I=1,N
      IF(I-K) 31,10,31
   31 W=A(I,K)
      DØ 30 J=K,N
      A(I,J)=A(I,J)-W*A(K,J)
   30 CØNTINUE
   10 CØNTINUE
      C=1.
      DØ 50 I=1,N
      C=C*B(I)
   50 CØNTINUE
      C=C*(-1.)**JJ
      GØ TØ 56
   55 C=1.0E-60
   56 RETURN
      END


ØBJ ØUTPUT END
```

Chapter 2

CMP

Chapter 2 MULTI-LINE METHOD

It has been pointed out that "Interference" in analytical atomic spectroscopy, which affects the spectral intensity received by the detector, can be classified into several kinds. The first is spectroscopic interference which is attributable to low resolution power of dispersion system, compared with that requisite for separating the neighbouring lines emitted from different lines. High resolution becomes particularly essential in AES with highly exciting sources. Stray light due to grating defect sometimes causes spectral interference, as exemplified by ICP analyses of samples containing a large amouts of Mg and Ca. The second is attributed to the change in the degree of atomization, caused by co-existing matrices. This is called chemical interference. The third and fourth are the interferences due to the changes in the excitation temperature, and degree of ionization of atoms of interest, caused by co-existing elements, respectively. Interelement effects may be partly attributable to such kinds of interference. Another is the interference due to the change in the nebulization efficiency, caused by the fluctuation in sample viscosity. This is sometimes called physical interference. Some other causes such as the change in the spatially distribution of species in atomizer and exciting source may be participant.

Up to date, however, these have been almost presumed only from the experimental results of the change in the spectral intensity [78, 79] and few clear evidence and elucidation have been reported. Naturally, no methods for correction of interferences have been proposed.

For these purpose, the author developed a novel method "Multi-line method." By comparing atomic and ionic lines or molecular lines assigned to the transition from the upper levels of different energy, the parameters associated with the excitation and ionization or atomization processes can be determined. Once knowing the mechanisms of the interferences, we can correct the interferences by using these parameters. Figure 1 demonstrates typical atomizer and exciting sources used in analytical atomic spectroscopy. They can be roughly categorized into three kinds, viz. chemical flames, discharge plasmas and ETA.

The chemical flames use fuel gases such as hydrogen, coal gas, propane and acetylene, and oxidizing gases such as air, oxygen, nitrous oxide and cyanogen [80]. Though there are many possible combinations of the fuel and oxidizing gases, air-hydrogen, air-acetylene and nitrous oxide-acetylene flames have been most commonly employed in practical analyses, from such viewpoints as the adequate combustion rate and obtainable high temperature. Owing to relatively high combustion rate, the hydrogen flames are usually supported by the Beckmann type (or total consumption type) burner, and called diffusion flame. Because of relatively low temperatures (up to ca. 2050°C) and low degree of atomization due to the direct introduction of large size droplets of sample solutions, the use of hydrogen flames has been limited to the analysis of relatively easily atomized elements such as lead in human blood and plasma samples. However, it has such advantage as to give low background absorption in AAS measurements. Because of relatively low combustion rate, the pre-mixing type of burner, in which larger size droplets of sample solution are removed, can be used for the air-acetylene flames. The removal of large size droplets and raised temperatures (up to ca. 2300°C) makes higher the degree of atomization in the air-acetylene flames than that in the air-hydrogen flames. For this reason, the air-acetylene flames have been most frequently used as the atomizer in AAS. Except such elements as Al, Si, Ti, V, rare earth elements etc. that form refractory compounds in the flame,

Fig. 1. Various types of atomizers and excitation sources

the air-acetylene flames are quite adequate for the atomization of most of metals. For the atomization of such elements, the nitrous oxide-acetylene flames are suitable because of higher temperatures up to ca. 2700°C [80]. However, much care must be taken to the poison of nitrous oxide and the explosive character of the flame. For alkali elements, the flames described above give so high temperatures that ionization of atoms also takes place, resulting in lowering the sensitivity and complex inter-element effects. In such a case, air-coal gas flames at lower temperatures (up to ca. 1900°C) are suitable. Except the last case, the inter-element effects encountered in the chemical flame atomizers are mostly attributable to the change in the degree of atomization of non-atomic species containing the element of interest. Therefore, the mechanisms of atomization process or inter-element effects can be traced by determining the degree of atomization. The degree of atomization can be determined by measuring the spectral intensities of relevant atomic and molecular lines, and processing them accoding to the multi-line method. In this chapter, such an approach is applied to the elucidation of an atomization process such as $CuCl \rightarrow Cu + Cl$ in an air-hydrogen flame, and an inter-element effect between chromium and iron in an air-acetylene flame. The latter is one of the typical chemical interferences found in AAS. It is very complex and has not been fully studied.

For non-metallic elements with high excitation energy or elements whose oxides have large dissociation energy, the chemical flames can not attain high temperatures enough for the atomization or excitation. In order to overcome this, various types of electric discharge plasmas have been developed. Conventional spark/arc sources also belong to this category. However, their unstability, mainly due to the rapid consumption of graphite electrodes and fractional vaporization of samples is not suitable for quantitative analyses. In order to obtain discharge stability, DC plasmas have been modified into a plasma jet [81] and DC glow discharges involving a Grimm lamp [82]. Despite the discharge stability, they have not been extensively used in practical analyses, except the use of the Grimm lamp for high concentration analysis of steels and alloys, and that of an improved DC arc plasma for solution analysis. This is partly because DC glow discharges can not establish high excitation temperatures (< 4000 K) and plasma jet sources with high linear velocity suffers from the difficulty in the sample introduction.

In order to overcome such problems, several types of rf discharge plasmas have been developed. Owing to the trapping effect of charged species by electric and magnetic fields alternated at a high frequency, high excitation temperatures can be attained. The rf plasmas can be roughly classified into the ICP and CMP from the difference in the fashion of energy supplying, and the so-called radio frequency plasma and microwave plasma from the difference in the frequency of the electromagnetic wave used as the energy source. The currently used rf plasmas involve rf ICP [85], microwave CMP [83] and MIP [84]. The latter two microwave plasmas are more efficient in energy consuption (40-400 W) than ICP's (a few kW), and give much less radiation interference with the other instrumental circuits. However, there arise problems associated with serious inter-element effects mainly due to the changes in the excitation and ionization processes. Nevertheless, the high efficiency of the microwave plasmas enables us to use gases with high metastable level energy as the plasma gas, leading to a possibility of highly sensitive analysis of elements with very high excitation energy. In practice, a helium MIP at atmospheric pressure have recently proved to allow analysis of halogens with a high sensitivity comparable to those for the other elements. In order to make the

Fig. 2. Model system of atomizers and excitation sources

microwave plasmas more useful, therefore, the elucidation and correction of the inter-element effect seems to be one of the most important subjects. In this chapter, the multi-line method is applied to a CMP. The mechanism of the inter-element effect on the manganese line intensity by alkali and alkaline earth elements is studied. In INTRODUCTION is described that ICP's suffer much smaller inter-element effects than CMP and MIP's, and also some presumption for this. In this chapter, the mechanisms of the small inter-element effects in ICP's also are discussed in connection with the inter-element effects in the CMP.

Several types of ETA have been developed for trace analyses of samples in a very small size (~ 50 mg), by L'vov [11], Massmann [12], West [13], Woodriff *et al.* Such ETA's have a capability to directly atomize various forms (solid, gel, suspension, emulsion etc.) of samples other than liquid. Sometimes more seriously than the chemical flame atomizers, however, the ETA's developed up to date suffer complicated chemical interferences mainly due to the change in degree of atomization and even sometimes due to that in vaporization mode. The key to reducing such effects seems to lie in prolonging the residence time of the resulting species in the atomizer and in making the species in the thermal and reaction equilibria. For the prolongation is suitable such a long tublar atomizer as the super high temperature GC separative atomizer [I116] as described in INTRODUCTION. In order to make the key obvious, the elucidation of the atomization mechanisms is inevitable. In this chapter, the multi-line method is applied to Massmann and West types of ETA. In such ETA's, the emission intensity strong enough for detection was not obtained for the atomic line of high excitation energy. Therefore, a method by AAS for the determination of the excitation temperature is developed.

2-1 Principle and Basic Theory

Figure 2 shows a model system of sample processing in atomizers and excitation source. In this system, any chemical pre-treatment processes are not included. As stated in INTRODUCTION, this is because the main subject of this section involves also the reduction of laborious pre-treatment procedures by direct atomization/excitation. Here, η is the efficiency of the sample introduction into the atomizers/excitation sources. If the sample introduction is made by nebulization, η mainly consists of such parameters as the sample uptake rate, the nebulization efficiency and the spatial distribution of sample aerosol or aerosol fraction in the atomizers/excitation sources. In the case of the ETA's, η chiefly involves such factors as those associated with the sampling device (micropipette microsyringe etc.), the vaporization rate, the spatial distribution in the ETA or the fraction within the section of spectroscopic observation. All of these factors vary depending on sample matrix. For instance, it has been reported that the nebulization efficiency decreases with the increase in the sample solution viscosity, as exemplified by the negative interference caused by a sulfuric acid matrix, encoutered in ICP-AES [22]. Despite its importance, no efficacious method has been proposed for this problem. In order to overcome the problem becomes necessary a certain method to control the nebulization process, such as particle couting/feedback control of an ultrasonic nebulizer. Unfortunately, the multi-line method also can not be applied to this problem. However, whether the parameter η is responsible for the interference or not can be clearly identified, since the other parameters can be determined by the multi-line method.

The sample introduced into the atomizer/excitation source is thermally dissociated to yield polyatomic molecules, diatomic molecules, atoms and ions either successively or concurrently. There can arise complicated reaction sequences in the atomizer/excitation source for practical samples containing a complex matrix. The multi-line method has such a theoretical features that the parameters concerning with the atomizer/excitation source, such as the fractions of species and the temperatures are, at first, spectroscopically determined, and that the individual reaction is subsequently examined. Therefore, the multi-line method requires only the thermal equilibria or Bolzmann's law conditions for the separate energy system (translational, vibrational, rotational and excitation systems) of the individual species, rather than the entire equilibria of the reaction and temperatures in a certain domain of the atomizer/excitation source. This makes the multi-line method quite suitable for practical system.

Each species is thermally (via bombardment or collision) excited to higher energy levels with the population according to the Bolzmann's law unless such a selective stimulation as that in AFS is present. Though the Fermi-Dirac's law strictly applies to the quantum system with discrete energy levels at lower temperatures, the Boltzmann's law is a good approximation for the system at higher temperatures than room temperature. Molecules have translational, rotational, vibrational and electronic systems. For each system, temperature can be defined and called translational, rotational, vibrational and electronic (excitation) temperatures, respectively. The former three temperatures are associated with the heat transportation and called gas temperature. In the system of atoms and ions, only the translational and excitation temperatures can be defined. These temperatures are the important parameters which represents the state in the atomizer/excitation source. Another important parameter is the fraction of each species. The fractions of atoms and ions are related to the degree of atomization and

ionization, respectively.

Each species emits, absorbs and fluoresces the resonance radiations (see Fig. 2). The multi-line method is based on the determination of the temperatures and fraction of the individual species by measuring and comparing the spectral intensity of the multi-lines of different term energy for the different species. The expressions developed below are mainly related to the emission phenomenon. However, they are applicable to the other phenomena viz. absorption and fluorescence if modified with the relevant basic theory.

The spectral intensity of the line emitted from a system can be expressed as (see also Fig. 2 in INTRODUCTION)

$$I_{nm} = h\nu_{nm} A_{nm} N_n$$

where I_{nm} is the spectral intensity for the transition between the upper level n and lower level n, h the Planck's constant, ν_{nm} the frequency of the emitted line, A_{nm} the Einstein's transition probability for the spontaneous emission and N_n the number of the species with the electron in the upper level. The transition probability A_{nm} can be given by the expression;

$$A_{nm} = (64\pi^4 e^2/hc^3)\, \nu_{nm}^3 \mid \mathbf{R}_{nm} \mid^2$$

where e is the electron charge, c the light velocity and R_{nm} the matrix element. The matrix element is given by the expression;

$$R_{nm} = \int \psi_n \mathbf{r} \psi_m \, d\tau \text{ and } \mathbf{r} = x\mathbf{i} + y\mathbf{j} + z\mathbf{k}$$

where ψ_n and ψ_m are the wave functions of the upper and lower levels, respectively, x, y, z the Cartesian coordinates, $d\tau = dxdydz$, and $\mathbf{i}$, $\mathbf{j}$ and $\mathbf{k}$ the unit vector. Therefore, the transition probability is determined by the wave functions of the participant levels.

The number of the species with the electron in the upper level N_n can be expressed by the Boltzmann's law;

$$N_n = N_s g_n \exp(-E_n/kT_s)/Q_s(T_s)$$

where N_s is the number of the species of interest, g_n and E_n the statistical weight and term energy of the upper level, respectively, k the Boltzmann's constant, T_s the temperature of the system of interest (e.g., the rotational temperature if the observed line is a rotational spectrum) and $Q_s(T_s)$ the partition function of the system of interest. The partition function $Q_s(T_s)$ can be given by the expression;

$$Q_s(T_s) = \sum_j g_j \exp(-E_j/kT_s)$$

which is the sum over states. By comparing the line intensity for the different upper level energy of the same system, we obtain the following expression;

$$I_1/I_2 = (\nu_1 g_1 A_1/\nu_2 g_2 A_2) \exp[(E_2 - E_1)/kT_s]$$

where the substripts 1 and 2 indicate the different two lines. From this expression, we can determine the temperature of the system of interest;

$$T_s = (E_2 - E_1)/k ln\ (I_1 \nu_2 g_2 A_2 / I_2 \nu_1 g_1 A_1).$$

This is the well-known "Ornstein's two line method" [184] which has been used for the spectroscopic measurements of temperatures in arc and spark plasmas. If the other multi-lines with different upper level energy are detectable, it gives better precisions to determine the temperature by plotting $\ln(I/\nu gA)$ against E/k (the Corliss' method [186]). The slope gives $-T_s^{-1}$ (see Fig. 3)

Fig. 3. Plot of ln $(\lambda I/gA)$ *vs.* E/k. Current for hollow-cathode lamp, 5 mA.

The number of individual species can be expressed as follows;

$$N_M = N_T \eta (1 - \beta - \chi)$$
$$N_A = N_T \eta \beta$$
$$N_I = N_T \eta \chi$$

where N_M, N_A and N_I are the number of the molecules, atoms and ions, which have the element of interest, respectively, N_T the total number of these species, η the sample introduction efficiency involving the nebulization efficiency, β the degree of atomization and χ the degree of ionization. In high power plasma excitation sources at high gas temperatures and atmospheric pressure, molecular species may be negligible in the number, i.e., $N_M = 0$. In such a case, the intensity of atomic and ionic lines becomes a function of the excitation temperatures, the degree of ionization and the total number of atoms and ions. The excitation temperature in the atomic system can be determined by the two line method, or measuring the relative intensity of two atomic lines of different upper energy. The excitation temperature in the ionic system also can be determined by measuring the relative intensity of two ionic lines of different upper energy. Then, the other parameter, viz. the degree of ionization χ can be determined by comparing the intensity of the atomic and ionic lines. By monitering the fluctuation in these parameters, viz. the excitation temperatures of atoms and ions, the degree of ionization, and the number of atoms and ions, we can trace the status changes in excitation/ionization processes and the origin of inter-element effects. Since two atomic lines and two ionic lines are measured, this method is named "Four line method" by the author. In chemical flames and ETA's at low temperatures, the degree of ionization is very low. For such a case, the approximation $N_M = N_T \eta (1 - \beta)$ can apply. By measuring the intensity of atomic lines and molecular lines, we can determine the temperatures, the degree of atomization and the

number of atoms and molecules. By monitoring the fluctuation in these parameters, we can trace the status changes in atomization/excitation processes, and the origin of chemical interferences.

The total number of the species containing the element of interest must be independent of the interferences caused in atomization/excitation processes. Therefore, the quantity N_T can be used for interference-free calibration instead of the spectral intensity. In this way, the correction of interferences can be made. If the correction can not apply, the causes partly involve the fluctuations in the sample introduction efficiency and the spatial distribution of the relevant species in the atomizer or exciting source, caused by the co-existing matrices.

2-2 Application to A Capacitively Coupled Plasma

In several types of emission source, there are inter-element effects in the excitation and ionization processes; practical applications have therefore been restricted to special cases. Recently, it has been proved that the inductively coupled plasma (ICP) has the advantage that such interference effects are much smaller than those given by other kinds of plasma source [87, 88].

The microwave-excited plasma torch also is of considerable interest in the determination of elements with high excitation energies. This technique, however, appears to suffer from interference phenomena caused by cations and free electrons resulting from elements which have ionization potentials lower than those of the elements of interest.

In this section, the multi-line method is applied to elucidation and correction of interferences from variations in the excitation temperature and the degree of ionization in a capacitively coupled plasma. This is also expected to be useful for the ICP when small inter-element effects change with the fluctuation in r.f. power or flow rate of carrier gas [89, 90]. However, it should not be applied to interferences arising from variations in nebulization [91] or atomization efficiency.

2-2-1 Theory

From the basic expressions are modified to apply for the system of atoms and ions.

The spontaneous emission intensity can be expressed for a transition (upper level 1 to lower level 1') by

$$I_{a1} = h\nu_{a1} A_{a1} N_{a1} \tag{1}$$

where h is Planck's constant, ν the frequency, A the Einstein transition probability for spontaneous emission, N_{a1} the number of atoms with an electron in the upper level 1, and the subscripts a and 1 indicate the atom and level number, respectively. Unless selective excitation occurs, the Boltzmann distribution can be applied to the energy system:

$$N_{a1} = N_a \frac{g_{a1}}{Q_a(T_a)} \exp(-E_{a1}/kT_a) \tag{2}$$

where N_a is the number of atoms, g_{a1} the statistical weight, E_{a1} the energy of the upper level, k the Boltzmann constant, T_a the excitation temperature and

$Q_a(T_a)$ the partition function equal to $\Sigma_j\, g_{aj} \exp(-E_{aj}/kT_a)$.

The number of atoms N_a can be replaced by $N_t(1-\chi)$, where N_t is the total number of atoms and ions and χ the degree of ionization. If the degree of atomization or the nebulization efficiency varies, N_t must be replaced by $N_s\eta\beta$, where η is the nebulization efficiency and β is the degree of atomization. However, this case is not dealt with here. Combining the above relationships gives

$$I_{a1} = h\nu_{a1}\, N_t(1-\chi)\frac{g_{a1}A_{a1}}{Q_a(T_a)}\exp(-E_{a1}/kT_a) \tag{3}$$

To determine the excitation temperature T_a, this equation is written for transitions with different upper energies, and the intensity ratio I_{a1}/I_{a2} is obtained. Rearrangement of this expression gives

$$T_a = (E_{a2}-E_{a1})/k\, \ln\left(\frac{\nu_{a2}g_{a2}A_{a2}I_{a1}}{\nu_{a1}g_{a1}A_{a1}I_{a2}}\right) \tag{4}$$

This is the well-known two-line method.

For the ionic system, the following equations can be introduced in the same fashion as for the atomic system. As the number of ions $N_i = N_t\chi$:

$$I_{i3} = h\nu_{i3}N_t\chi\,\frac{g_{i3}A_{i3}}{Q_i(T_i)}\exp(-E_{i3}/kT_i) \tag{5}$$

where the subscript i stands for ion. Thus

$$T_i = (E_{i4}-E_{i3})/k\, \ln\left(\frac{\nu_{i4}g_{i4}A_{i4}I_{i3}}{\nu_{i3}g_{i3}A_{i3}I_{i4}}\right). \tag{6}$$

These two equations are valid independently of the values of η, β and χ.

The degree of ionization χ can be determined by taking a ratio I_a/I_i or I_i/I_a:

$$\frac{I_a}{I_i} = \frac{\nu_a g_a A_a Q_i(T_i)\,(1-\chi)}{\nu_i g_i A_i Q_a(T_a)\chi}\exp\left(\frac{E_i}{kT_i}-\frac{E_a}{kT_a}\right) \tag{7}$$

Any combination between the atomic and ionic lines is allowed, e.g., I_{a1}/I_{i3}, I_{a2}/I_{i3}, I_{a1}/I_{i4} or I_{a2}/I_{i4}. Consequently,

$$\chi = \left[1+\frac{I_a\nu_i A_i g_i Q_a(T_a)}{I_i\nu_a A_a g_a Q_i(T_i)}\exp\left(\frac{E_a}{kT_a}-\frac{E_i}{kT_i}\right)\right]^{-1} \tag{8}$$

From eqns. (3) and (5), N_t is given by:

$$N_t = I_i\,\frac{Q_i(T_i)}{h\nu_c\chi g_i A_i}\,\exp(E_i/kT_i) \tag{9}$$

and

$$N_t = I_a\,\frac{Q_a(T_a)}{h\nu_a(1-\chi)g_a A_a}\,\exp(E_a/kT_a) \tag{10}$$

Equation (10) is suitable for small values of χ, and eqn. (9) for large values.

The partition functions for the atomic and ionic systems have been obtained for various elements, developed in the form of a series [92]. Thus, if the intensities of four lines I_{a1}, I_{a2}, I_{i3} and I_{i4} are measured experimentally, the total number of atoms and ions N_t can be determined.

Manganese was chosen as the element to be measured because intense radiation was observed for the four lines required. The lines selected and their

physical properties are listed in Table 1 [93]. The atomic and ionic partition functions for manganese are: [92]

$$Q_a(T_a) = 5.7492 + 0.36614\,(T_a/10^3) - 0.17998\,(T_a/10^3)^2 + 0.031845\,(T_a/10^3)^3 + 0.000991\,(T_a/10^3)^4$$

$$Q_i(T_i) = 6.9764 + 0.09951\,(T_i/10^3) - 0.09092\,(T_i/10^3)^2 + 0.027782\,(T_i/10^3)^3 - 0.001495\,(T_i/10^3)^4$$

TABLE 1

The four lines selected and their properties

Wavelength (nm)	Upper energy (cm^{-1})	gA value ($10^6\ s^{-1}$)	Response factor
Mn(I) 403.08	24,802	1.4	5.9
Mn(I) 279.48	35,770	8.3	8.4
Mn(II) 294.92	43,370	66	9.0
Mn(II) 260.57	38,366	33	8.0

2-2-2 Experimental

Apparatus

A Hitachi UHF plasma torch spectrometer Model 300 [83] was used for the excitation source. It forms a capacitively coupled plasma supplied by microwave power of 300—400 W at 2450 MHz. In order to avoid interferences from variations in efficiency, a desolvation system was not incorporated in the sample-introducing system and the nebulizer was fitted directly to the plasma cavity. A brass cone for mounting the aluminum discharging electrode was replaced by an aluminium cone to avoid contamination when acidified sample solutions were used. Spectral measurements were made through a small rectangular aperture constructed by an additional slit of 2.0-mm width located in front of the entrance slit of the monochromator. The profile of the plasma torch was imaged onto the slits with a magnification ratio of unity.

The working conditions for the plasma torch are listed in Table 2. To stabilize the plasma discharge, small amounts of nitrogen were mixed with the argon. However, too much nitrogen rapidly damaged the aluminum electrode.

In order to estimate the characteristics of the plasma, the other gases, nitrogen and carbon dioxide also were used as the plasma supporting gas.

Reagents

A stock standard solution of manganese (100 μmol ml^{-1}) was prepared by dissolving manganese metal in distilled hydrochloric acid. The solution was diluted with distilled deionized water to 10 μmol ml^{-1} just before use. The acidity of the solution was adjusted to 0.1 M.

Stock standard solutions of the interfering elements were prepared by dissolving their reagent-grade carbonates in distilled hydrochloric acid. They were added to the manganese solution before dilution.

To estimate the net intensity, the instrumental response was divided by a response factor. The factor is a product of the efficiency of the grating and the quantum yield of the photocathode in the photomultiplier tube. These

depend on the wavelength. Figure 4 shows the response factor for the combination of a grating of blaze wavelength 250 nm (Hitachi) and photomultiplier tube R106 (HTV). The response factors for each of the four lines are listed in Table 1.

TABLE 2

Working conditions for plasma and spectrometer

Flow rate of nebulizing gas	1.5 l min^{-1}
Flow rate of plasma sheath gas	3.5 l min^{-1}
Field current for magnetron	400 mA
Anode current for magnetron	300 mA
Entrance slit width	30-50 μm
Exit slit width	30-50 μm
Measurement position	7-25 mm above electrode

Fig. 4. Variation of instrumental response factor with wavelength.

2-2-3 Characterization of plasma

In order to estimate the basic characteristics of the plasma, the distribution of the excitation temperature and the degree of ionization of manganese atoms were examined, prior to the elucidation of the inter-element effects.

Distribution of excitation temperature

A 10^{-2} M manganese solution was steadily nebulized into the plasma torch.

The emission was observed through slits (30 μm wide and 1 mm high), so that the emitted light was observed as an average intensity over the rectangle.

Flow rates of gases were held constant at *ca.* 5 ℓ min^{-1}, and the pressure of nebulization was maintained constant (2 Kg cm^{-2}). The microwave power supply was about 250 W for argon or nitrogen plasma. However, when carbon dioxide was introduced, the plasma could not be maintained, and the aluminum electrode was exhausted by oxygen radicals; resulting aluminum oxide decreased the efficiency of the microwave radiation and made the plasma unstable. Accordingly, a larger power supply (*ca.* 450 W) was required to maintain the plasma, and prolonged observations were impossible. Under the optimal conditions, the excitation temperature was about 3800 K even in the hottest region. Apparently, the torch furnished by carbon dioxide was the smallest; the torch with nitrogen was larger and that with argon the largest.

The excitation temperature profiles observed in the argon plasma torch and in the nitrogen torch are shown in Figs. 5 and 6, respectively. The results show that the excitation temperature was higher in the argon plasma than in the nitrogen one, which may be due to the vibration of the nitrogen molecule.

Part of the radiated microwave energy is finally distributed among the

Fig. 5. Profile of excitation temperature of manganese atoms in argon plasma torch.

Fig. 6. Profile of excitation temperature of manganese atoms in nitrogen plasma torch.

energies of vibration, rotation, translation and transition which appertain to various species in the plasma. If there is a thermal equilibrium in a system of species i, the energy of the system $e_i = (N_i/Q_i) \sum_j e_{ij} \exp(-e_{ij}/kT_i)$. When the whole system is in equilibrium, T_i is independent of i. The total energy must be constant when the plasma is regularly supplied with the microwave power, hence the larger N_i, the smaller T_i. Temperatures of other systems can be affected by N_i as far as energy transfer is concerned, even when perfect equilibrium is not achieved throughout the system. Therefore, temperatures decrease when molecules possessing a high degree of freedom are introduced into plasma: the effect decreases for different plasmas in the order argon > nitrogen > carbon dioxide.

With regard to the gradient of the excitation temperature, the middle in the plasma torch had a planar region and the circumference a steep precipice, which suggests disequilibrium in the tail region.

Distribution of degree of ionization

Under the same conditions as described above, the degree of ionization of manganese atoms in the plasma was determined.

The ionic lines of manganese were hardly detectable when carbon dioxide was introduced. The observed profiles in argon and nitrogen plasmas are shown in Figs. 7 and 8, respectively. The degree of ionization in nitrogen plasma declined (60% to 10%) as the electron temperature fell (3700 K to 2900 K); in the argon plasma a maximum occurred about 4 mm from the central axis and 22 mm above the electrode, which indicates that at the root of the torch, argon lacking vibrational or rotational energy does not yield sufficient energy.

Further evidence was provided by other systems. In Figs. 9 and 10 are shown the relative intensities of strontium lines (from $SrCl_2$) and boron (from H_3BO_3), respectively. The emission intensity of boron in nitrogen plasma was similar to that in argon plasma; probably, boric acid is easily

Fig. 7. Profile of degree of ionization of manganese atoms in argon plasma.

Fig. 8. Profile of degree of ionization of manganese atoms in nitrogen plasma.

Fig. 9. Relative intensity of strontium lines (Sr(I) 467.03 nm, Sr(II) 407.77 nm). (A) Sr(II) in argon plasma torch, (B) Sr(I) in argon one, (C) Sr(I) in nitrogen one, (D) Sr(II) in nitrogen one.

Fig. 10. Relative intensity of boron line (249.77 nm). (A) Argon plasma torch, (B) nitrogen one.

dissociated in nitrogen plasma so that dissociation is the predominant reaction, whereas strontium is easily dissociated in argon plasma and high temperature is important insofar as ionization does not predominate. But higher temperatures increase ionization, causing weaker atomic lines and stronger ionic lines.

Distribution of total number of atoms and ions

Equation (10) was used to estimate the relative distribution of the total number of atoms and ions. In practice, however, as the torch varied in thickness along its length, a correction based on a cylindrical state was made. The horizontal and vertical distributions determined in this way are shown in Fig. 11.

The results indicate that in the horizontal plane the verges of the torch have a higher species concentration than the center, but that the maximum occurs in a vertical direction. There is therefore a problem that the sample aerosol cannot be thoroughly mixed with the plasma.

Fig. 11. Relative number of manganese atoms and ions in nitrogen plasma torch. (A) Vertical distribution. (B) horizontal distribution.

2-2-4 Elucidation and correction of inter-element effect

As shown by the theory in Sec. 2-3-1, the factors, which are responsible for the change in the spectral intensity caused by the inter-element effects, are the excitation temperatures of atoms and ions, and the degree of ionization of atoms of interest. The variation in these factors were monitored by the four line method to elucidate and correct the inter-element effect. As typical examples, manganese and alkali or alkaline earth elements were chosen as the elements suffering and causing the inter-element effect, respectively. In order to change the ionic strength or the density of free electrons, their concentrations were adjusted in two fashions; a constant molar concentration of manganese ($10\,\mu mol ml^{-1}$) with varied concentrations of the interfering elements, and a constant total molar concentration of manganese and the interfering element (total concn. = $10\,\mu mol ml^{-1}$) with varied ratios. For these two cases, contrary shifts (enhance or decrease) were found in the excitation temperatures of atoms and ions, with the increase in the concen-

tration of the interfering elements. The inter-element effects on the emission intensity of the analytical lines of the other elements by alkali and alkaline earth elements also were examined. The obtained results are discussed in relation to the above results and the known characteristics of ICP's.

Finally, the four line method is applied to the correction of the inter-element effect in the manganese-alkaline earth element system.

Elucidation of inter-element effect

Figure 12 shows the inter-element effect caused by alkali and alkaline earth elements on the excitation temperatures of atoms and ions of manganese, and the degree of ionization of manganese atoms, which were determined by the four-line method. Here, the concentration of manganese was kept constant. As for the results in Figs. 12 ii)-iv), the excitation temperature of manganese atoms is lower than those in Fig. 12 i), because small amounts of nitrogen gas was mixed in argon gas to stabilize the CMP. It can be seen from these figures that the excitation temperature of manganese atoms decreases with the increase in the concentration of the interfering elements, and that the decrease in the excitation temperature is more seriously caused by the interfering element with a lower ionization potential (see also Table 4). Figures 12 ii)-iv) indicate also that the excitation temperature of manganese ions increases with the rise of the concentration of the interfering elements. Figure 13 shows the inter-element effect on the degree of ionization. It can been seen from this that the degree of ionization of manganese atoms significantly decreases with the increase in the concentration of the interfering elements. In this case, both atomic and ionic line increased in spectral intensity with the increase in the concentration of the interfering elements. From these results, the inter-element effect in this case can be elucidated as follows. The increase in the atomic line intensity can be attributed mainly to the increase in the number of neutral atoms of manganese with the decrease in the degree of ionization, which prevails against the depressing effect caused by the decrease in the excitation temperature of manganese atoms. The increase in the ionic line intensity may be attributed chiefly to the increase in the excitation temperature of ions, which prevails against the depressing effect caused by the decrease in the number of ions. Which depressing or enhancing effect is pre-eminent could be determined by the difference in the magnitude of the upper level energy of the element suffering the inter-element effect. In the latter case of the ionic lines, the parameter associated with the excitation may prevail while in the former case of the atomic lines the parameter associated with the degree of ionization may prevail, since the upper level energy of the ionic lines is higher than that of the atomic lines.

The decrease in the degree of ionization of manganese atoms can be elucidated with the LeChatelier's law or the shift in the equilibrium of the ionization reaction according to the mass action law;

$Mn \rightleftarrows Mn^{+} + e$

$Int. \rightleftarrows Int.^{+} + e$

where Int. indicates the interfering element. With the increase in the concentration of the interfering element, the concentration of the free electrons increases, leading to the decrease in the degree of ionization of manganese atoms. With the addition of the interfering element with the lower ionization potential, the higher density of the free electrons is attained, resulting in the

Fig. 12. Effects of alkali and alkaline earth metals on the excitation temperatures of manganese atoms and ions; (A) Lithium added, (B) sodium added, (C) potassium added, (D) calcium added, (E) strontium added

The concentration of Mn is kept constant.

Fig. 13. Effects of alkali and alkaline earth elements on the degree of ionization of manganese atoms

more serious depression of the ionization of manganese atoms. This elucidation can not apply if the reaction equilibria are not attained. Some kinetic examination becomes necessary. In such a case the other mechanisms may also be likely. At any rate, it is the experimental evidence that the decrease in the degree of ionization of manganese atoms is caused by a certain process with the presence of the interfering element, since the four line method can be applied to the determination of the quantity without any assumption of the reaction equilibria. The decrease in the excitation temperature of manganese atoms can be called, in other words, deactivation of manganese atoms. The cause for the deactivation is not clear. Direct energy transfer from the excited manganese atoms to the interfering atoms through collisions is not very likely unless their level energy approximates to each other in magnitude. The excitation temperatures is lowered with the addition of nitrogen gas which has the systems (vibration and rotation) other than translation and electronic systems for the energy distribution. In a similar fashion, the addition of the interfering elements might cause the auxiliary energy distribution to the excitation and ionization of them, leading to less energy distribution to the electronic system of manganese atoms. The decrease in the excitation temperature caused in such a fashion might become more serious in lower energy plasmas. This will be also discussed later on the decrease in the intensity of H_β line, OH band and continuum. The most difficult problem to explain is the increase in the excitation temperature of manganese ions. The discussion described above can not be applied to this case. Some species resulting from or indirectly induced by the interfering elements, free electrons?, might excite the manganese ions. Detailed discussion could be made if the cross section of excitation by collisions can be estimated.

Figures 14 and 15 demonstrate the results for the case of the constant total molar concentration of manganese and interfering element. Figures indicate also the changes in the excitation temperature and the degree of ionization of the interfering atoms. Their physical properties are listed in Table 3. As in the case of the constant manganese concentration with the varied concentration of the interfering elements, the degree of ionization of manganese atoms decreases with the increase in the concentration of the interfering elements, and the decrease becomes more serious for the interfering element with a lower ionization potential. However, it is noteworthy

that the changes in the excitation temperatures of atoms and ions of manganese are contrary to those in the preceding case, i.e., that the excitation temperature of manganese atoms increases with the increase in the concentration of the interfering elements while the excitation temperature of manganese ions slightly decreases. The decrease in the degree of ionization of

Fig. 14. Excitation temperature observed. (•) Manganese atoms: (1) barium added, (2) calcium added, (3) strontium added, (4) magnesium added. (A) Barium ions, (B) strontium atoms, (C) calcium atoms, (D) magnesium atoms, (E) manganese ions (for each additive).

Fig. 15. Degree of ionization observed. (•) Manganese atoms: (1) barium added, (2) strontium added, (3) calcium added, (4) magnesium added. (A) Barium atoms, (B) strontium atoms, (C) magnesium atoms, (D) calcium atoms.

manganese atoms might be elucidated as in the preceding case. However, the reason why the excitation temperatures change contrarily is very difficult to explain. Possible causes might involve that the change in the density of free electrons varies the cross section in the excitation processes of atoms and ions. Thus, the overall inter-element effect on the spectral intensity can become very complicated.

Figures 16 and 17 show the effect of the interfering elements on the spectral intensity for the OH emission, the H_β line, the argon line and the continuum background emission. All of the optical energies are depressed by the addition of the interfering elements, and the effect is more serious for the interfering element with a lower ionization potential. This suggests that the energy is distributed to the extra system, i.e., the excitation and ionization of the interfering elements, and consequently that the energy shares to the observed systems decrease. In practice, the core of argon plasma torch apparently became smaller when the interfering elements were added.

Figure 18 demonstrates the inter-element effect on the spectral intensity for various elements with a different ionization potential. The atomic emission intensity for elements with a relatively lower ionization potential, such as Sr, Cr and V suffer the enhancing effect similar to those for the

TABLE 3

LINES OBSERVED

Element	*Wavelength (nm)*	*Upper energy (cm^{-1})*	*gf-value*
Mn I	403.1	24,802	0.33
I	279.5	35,770	3.4
II	257.6	38,807	7.9
II	294.9	43,370	8.6
Mg I	383.8	47,957	8.6
I	285.2	35,051	1.1
II	279.6	35,761	1.1
II	280.3	35,669	0.62
Ca I	445.5	37,757	2.2
I	422.7	23,625	0.28
II	396.9	25,192	0.11
II	393.3	25,414	0.21
Sr I	460.7	21,698	0.27
I	487.6	35,400	0.47
II	407.8	24,517	0.17
II	421.6	23,715	0.10
Ba I	553.6	18,060	0.9
II	493.4	20,262	0.068
II	413.1	46,155	4.6

TABLE 4 First ionization potential

Element	I.P. (eV)	Element	I.P. (eV)
Li	5.39	V	6.74
Na	5.14	Cr	6.77
K	4.34	Sb	8.64
Mg	7.65	B	8.30
Ca	6.11		
Sr	5.69		
Ba	5.21		

Cited from "Lange's handbook of chemistry" by N.A. Lange, 12th Ed., 1934, McGraw-Hill Book Co., Tokyo.

manganese lines. As for antimony with a higher ionization potential, the inter-element effect turns from enhancing to depressing at a higher concentration of the interfering element, sodium. Consequently, there arises a maximum on the curve. This may be explained as follows. At the lower concentrations of sodium, the decrease in the degree of ionization prevails to give the enhancing effect while at the higher concentrations, the decrease in the excitation temperature of atoms become significant to result in the depressing effect. As for the boron line, there exists the depressing effect alone. The ionization potential of boron is slightly lower than that of anti-

mony (Table 4). On the other hand, the upper level energy of the boron line is higher than that of the antimony line. In this case, the decrease in the excitation temperature of boron atoms dominantly affects the spectral intensity, since the term of the excitation temperature is exponential (see the theoretical equations in Sec. 2-1). Therefore, it can be suggested that whether the inter-element effect is enhancing or depressing can be altered by the differences in such parameters as the ionization potential and the excitation energy of the element suffering the inter-element effect, those of the interfering elements, total ionic strength and the density of free electrons.

Here, some discussion on ICP's is made in connection with that described

Fig. 16. Effect of potassium (a) on OH emission (306.4 nm), (b) on H_β line, (c) on argon line (394.8 nm). (O---O) Horizontal distribution, (O---O) vertical distribution. (A and D) No potassium added, (B and E) 15 μmol K ml^{-1} added, (C and F) 30 μmol K ml^{-1} added.

Fig. 17. Effect of alkali and alkaline earth elements on OH emission (306.4 nm) and continuum background emission (280.0 nm). (A) Lithium added, (B) sodium added, (C) potassium added, (D) calcium added, (E) strontium added and (F) magnesium added.

Fig. 18. Effects of sodium on emission intensity of various elements. (a) Sr(I), 460.7 nm; (b) Sr(II), 407.8 nm; (c) Cr(I), 425.4 nm; (d) V(I), 437.9 nm; (e) B(I), 249.8 nm; (f) Sb(I), 231.1 nm. (A) Argon plasma torch, (B) nitrogen torch.

above. In order to scrutinize the mechanisms of the ICP, Kawaguchi *et al.* [118], utilizing a photodiode array detector, measured the changes in spatial profile of spectral intensity for various elements such as Cs, Al and Cu, which were caused by the inter-element effects. It was pointed out that the enhancing effects by alkali elements were found in the lower positions (< ca. 15 mm) of measurement above the rf working coil, while the depressing effects at the higher positions (> ca. 20 mm). Near a region of 15-20 mm above the rf coil, the enhancing and depressing effects are neutralized each other. Usually, this region is used as the optimum measurement position for the analysis with low inter-element effects. It has been pointed out that the low inter-element effects in ICP's are partly attributable to the high density of free electrons caused by the Penning ionization. In practice, the high density free electrons can act as a buffer for the fluctuation in the equilibrium of the ionization reaction, leading to the low inter-element effect [I124, I125]. However, this seems to be based only on the estimation of a bulk characteristic of ICP's. As shown by the spatial profile study [118], the practical status appears to be not simple. The key seems to lie in that the circumstance, which atoms actually experience in a certain domain can be reflected on the behaviour of the spectral intensity in the domain. From such a viewpoint, the following mechanisms could be deduced. In the lower region, the sample matrix involving solvent is not completely decomposed into atomic species. Consequently, the slow free electrons in plasma can be trapped by high electron affinity species such as OH, halogen atoms etc. As result, the density of free electron decreases. In such a circumstance become likely the enhancing effect due to the decrease in the degree of ionization of atoms. In the higher position, the density of free electron is higher, since the sample is supplied with a sufficient energy when passing through the plasma, to decompose thoroughly. Therefore, the enhancing effect is absent. However, the depressing effect due to the decrease in excitation temperature still remains. This effect may be caused also in the lower region. Thus, in the optimum region, the enhancing and depressing effects can cancel each other. Therefore, such neutralization position can vary with the difference in sample kinds. In practice, the optimum measurement position has been reported to vary slightly with the element of interest. However, more experimental evidences are necessary for the complete elucidation of the ICP mechanisms. The multi-line method is also useful for the research of the ICP mechanisms.

Correction of inter-element effect

Once the excitation temperatures and the degree of ionization are measured by the four-line method, we can determine the total number of atoms and ions, which is independent of the inter-element effect. We can use this parameter for the calibration instead of the spectral intensity. The correction of inter-element effect can be thus made.

For practical purposes, the radiation was observed at a defined sectional point and the Abel transformation [94] was not applied in the calculation.

Figure 19 shows the dependence of the excitation temperatures of manganese atoms and ions (T_a and T_i) on the concentration of strontium. There is no local thermal equilibrium between the atomic and ionic systems, and the excitation temperatures change significantly with the concentration of strontium. The change suggests that energy is transferred to the manganese ionic system

and removed from the manganese atomic system.

Figure 20 demonstrates the dependence of the degree of ionization, χ, on the concentration of strontium. Ionization is suppressed by the presence of strontium. This phenomenon is similar to those encountered for a nitrous oxide—acetylene flame in atomic absorption spectrometry [95], which are attributed to changes in equilibrium between the ionization processes of the two elements. Detail discussion is given in the preceding section.

However, regardless of the physical mechanisms, it is possible to correct the interference if the excitation temperatures and the degree of ionization are determined. Figure 21 shows the dependence of the uncorrected intensity of the atomic radiation and the corrected value, i.e. the total number of atoms and ions N_t, on the concentration of the interfering element. The former is strongly affected by strontium as a result of the variation in the ex-

Fig. 19. Dependence of the manganese excitation temperatures on strontium concentration: T_a atomic, T_i ionic excitation temperature.

Fig. 20. Dependence of the degree of manganese ionization on strontium concentration.

Fig. 21. Corrected and uncorrected responses for manganese in the presence of strontium.

citation temperature and the degree of ionization. In spite of such a strong interference effect, the corrected value remains essentially unaffected by the strontium concentration.

Symmetry in the plasma torch

There is a problem concerned with the symmetry of spatial distribution of spectral line intensity in the plasma torch. Figure 22 depicts the projected profile of the intensity distribution for the atomic line Mn(I) 403.08 nm after successful correction. The distribution is reasonably symmetrical. Figure 23, however, demonstrates that when lithium or barium is the interfering element, the corrected distributions are asymmetrical. The corresponding dependences of the excitation temperature and the degree of ionization are illustrated in Fig. 24 and 25, and the corrected results in Fig. 26. The correction fails in both cases. It should be pointed out that there are inflection points on the excitation temperature curves for atoms or ions in the presence of these elements.

Fig. 22. Profile of the intensity distribution for 10 μmol Mn ml^{-1} + 5 μmol Sr ml^{-1}.

Fig. 23. Profile of the intensity distribution for 10 μmol Mn ml^{-1} + 5 μmol Li ml^{-1} (•) or 5 μmol Ba ml^{-1} (○).

Fig. 24. Dependence of (a) the manganese excitation temperatures and (b) the degree of manganese ionization on lithium concentration.

Apparently, the plasma torch was supported asymmetrically about the co-axis of the discharging and cylinder electrodes, and an anomalous discharge to the cylinder electrode partly occurred. This lack of symmetry in the plasma torch causes the asymmetrical profile of the spectral intensity and the anomalous inflection on the excitation temperature curves. An error in the calculated temperature leads to a significant error in the total number of atoms and ions on calculating the exponential terms involved, which would be increased by the effect of lack of symmetry increasing an error from the net value determined by the Abel transformation. It was reported earlier that for a plasma such as an ICP in which the sample is introduced into a narrow region near the central axis of discharge, the Abel transformation is not necessarily required for measurement of the excitation temperature in the central region [96] . From this point of view, therefore, the present correction method is expected to be most promising if used with the ICP source.

However, the type of plasma supplied with low-power microwaves [97] and fitted with an electrothermal atomizer, seems to be a useful technique, for example, for microbiological samples, because its sample requirement is very small. This type of plasma also suffers from interferences connected with

Fig. 25. Dependence of (a) the manganese excitation temperatures and (b) the degree of manganese ionization on barium concentration.

Fig. 26. Corrected and uncorrected responses for manganese in the presence of (a) lithium and (b) barium.

excitation and ionization processes [97] . This type of plasma is supported within the quartz capillary, so that it forms a relatively symmetrical intensity profile. If the system is evacuated, high temperatures for the atomic and ionic systems are established. Therefore, the lines utilized for correction are increased in intensity. This feature is expected to make the correction method versatile enough for the determination of other elements.

For on-line measurement of the intensity of the four lines, a rapid scanning monochromator coupled to a microcomputer is under development. This will be described at a later date.

2-3 Application to Chemical Flame Atomizers

In the preceding section, the four-line method is applied to the elucidation of the excitation and ionization processes in the exciting source used for atomic emission spectroscopy. In this section, this method is applied to the studies of the mechanisms of the atomization processes or inter-element effect in an air-hydrogen flame and an air-acetylene flame, which have been most frequently used as the atomizer in AAS.

2-3-1 Atomization process of CuCl→ Cu + Cl in an air-hydrogen flame

As described in the previous sections, the inter-element effects encountered in the atomizers for AAS are mainly attributable to the change in the atomization processes or degree of atomization. In this section, the degree of atomization of CuCl is determined as a model by the multi-line method since the species CuCl emits a strong band spectrum in an air-hydrogen flame. The green band spectrum has been used for checking the presence of chlorine in materials with eyes (so-called Beilstein test).

Calculation

The temperature was measured by the well known two-lines method; two atomic copper lines which are of different upper-state energies were used:

$$T = E_1 - E_2/\ln(R_2/R_1) + \ln(\lambda_2 g_1 A_1 p/\lambda_1 g_2 A_2) \tag{1}$$

where T is the temperature in K, E_1 and E_2 are the upper energies, R_1 and R_2 the responses measured, λ_1 and λ_2 the wavelengths, g_1 and g_2 the statistical weights, A_1 and A_2 the Einstein transition probabilities for emission, and p is the factor for the response of the photomultiplier.

As in the previous treatment for the degree of ionization, the ratio of the copper and CuCl emissions can be expressed as follows:

$$pR_{Cu}/R_{CuCl} = \frac{\beta\lambda_{CuCl}Q(T)_{CuCl}g_{Cu}A_{Cu}}{(1-\beta)\lambda_{Cu}Q(T)_{Cu}g_{CuCl}A_{CuCl}} \exp\left(\frac{E_{CuCl}-E_{Cu}}{kT}\right) \tag{2}$$

where $Q(T)$ is the partition function. $Q(T)_{CuCl}$ is expressed as a product $q_v(T)q_e(T)$ for the line including all rotational lines, which constitute the P- and R-branches. The vibrational and electronic partition functions are written as follows, respectively:

$$q_v(T) = e^{-hc\omega_0/2kT}/1 - e^{-hc\omega_0/kT} \tag{3}$$

$$q_e = \sum_j g_j \exp(-E_j/kT) \tag{4}$$

where h is Planck's constant, c the light velocity, ω_0 the wave number of the fundamental vibration, and E_j the energy of state j. $q_e(T)$ was calculated, on the assumption that $g_j = 1$, from Table I, and $Q(T)_{Cu}$ was taken from the results of De Galan *et al.* . For $g_{CuCl}A_{CuCl}$, an approximate calculation for Σ–Σ and 0–0 transitions was carried out: [92]

$$g_{CuCl}A_{CuCl} = \frac{64\pi^4}{3h\lambda^3_{CuCl}} \mu_e^2 \left(\int \psi^2_{v=0}\, dx\right)^2$$

where the second term is unitary. The electronic transition moment μ_e was calculated, without regard to the overlapping integral $\mu_e = eab\, r_e$, where e is the electron charge, and a and b are coefficients in the wave function of the ground-state CuCl:

$$\psi^0_{CuCl} = a\phi_{Cu} + b\phi_{Cl} \tag{5}$$

and without regard to the overlapping integral, $a^2 + b^2 = 1$. Furthermore, in order to estimate a and b, use was made of the Pauling's electronegativities of copper and chlorine. The charge on the copper atom $q_{Cu} \approx \int 2\psi^{0^2}_{CuCl}\, dv \approx 2a^2$. q_{Cu} may be expressed in terms of the electronegativities χ_{Cl} and χ_{Cu} as follows:

$$q_{Cu} = e[1 - \exp\{-(\chi_{Cl} - \chi_{Cu})^2/4\}] \tag{6}$$

The results estimated were as follows:
$q_{Cu} = -q_{Cl} = 0.26e$, $a = 0.608$, $b = 0.794$ and $\mu_e = 2.51 \cdot 10^{-35}$ in c.g.s. with $r_e = 2.16$ Å.

Lines observed

The copper lines observed were those which had different upper energies; the observed CuCl emission line was a Σ–Σ transition with $v = v' = 0$. These are asterisked in Table 1.

TABLE 1

LINES PROPERTIES

Cu I			*CuCl emission*			
λ (nm)	*E (cm⁻¹)*	*gA (10⁸ s⁻¹)*	*λ₀,₀ (nm)*	*E (cm⁻¹)*	*ωₑ (cm⁻¹)*	*Transition*
327.4*	0–30535	1.9	395.8	0–25282	383	F–$^1\Sigma$(X)
249.2*	0–40114	0.31	433.4*	0–23077	406	$^1\Sigma$–$^1\Sigma$(X)
282.4	11203–46598	3.1	435.5	0–22973	395	$^1\pi$–$^1\Sigma$(X)
296.1	11203–44963	0.97	484.8	0–20635	399	C–$^1\Sigma$(X)
261.8	11303–49383	4.3	488.3	0–20488	401	B–$^1\Sigma$(X)
			526.4	0–19001	410	A–$^1\Sigma$(X)

With all values of constants inserted, eqn. (2) can be written as follows:

$$\beta = 1 - 1/1 + 0.66 \frac{R_{Cu,327.4}}{R_{CuCl,433.4}} f(T) \tag{7}$$

with the modified eqn. (1)

$$T = 13{,}807/\ln(R_{327.4}/R_{249.2}) - 1.897\,. \tag{8}$$

where

$$f(T) = \frac{2.598e^{-0.2999/T'}}{1 - e^{-0.5998/T'}} \frac{q_e(T')}{Q_{Cu}(T')} \exp(-11.02/T')$$

and

$$T' = T/1{,}000. \tag{9}$$

According to the result of De Galan *et al.*[92]

$$Q_{Cu}(T') = 2.1905 - 1.938 \cdot 10^{-1} T' + 5.1491 \cdot 10^{-2} T'^2 - 1.4419 \cdot 10^{-3} T'^3$$

and

$$q_c(T') = 1 + \exp(-36.37/T') + \exp(-33.20/T') + \exp(-33.05/T') + \exp(-29.69/T') + \exp(-29.48/T') + \exp(-27.34/T'),$$

which was derived directly from the definition with Table 1 on the assumption that $g_j = 1$.

Experimental

A Nippon Jarrell-Ash AA-1E atomic absorption and flame emission spectrometer was fitted with a Beckman-type burner and the response was recorded on a Hitachi QPD-54 recorder.

A 0.095 *M* copper solution was prepared by dissolving copper (II) chloride (analytical grade) in deionized water.

Fig. 1. Spectrum of CuCl. Slit width, 50 μm; air, 3 l min^{-1}; hydrogen, 15 l min^{-1}; aspirating rate, 0.40 mmol min^{-1}.

Figure 1 shows the observed CuCl spectrum. Figure 2 demonstrates the intensity distributions above the burner top for the Cu I lines and the CuCl emission. From the figure, any information for the atomization process can not be obtained. Figure 3 shows the excitation temperature of copper atoms and the degree of atomization of CuCl molecules. In the tail region of the flame, the excitation temperature is higher. However, the degree of atomization is higher in the lower region of the flame. This suggests that the reductive power of the flame in the lower region promotes the atomization of CuCl molecules. In the lower region, active hydrogen atoms may be rich. In the tail region, copper atoms are given more energy from the combustion

heat, resulting in the higher excitation temperature. The thermal energy also contributes to the atomization. In this case, however, the reductive power prevails against it. The principal reduction may be CuCl + H (H_2) → Cu + HCl + (H).

Fig. 2. Intensity profiles above the burner nozzle for CuI and CuCl emission. Air, 3 l min⁻¹; hydrogen, 9 l min⁻¹. (○) CuI, 327.4 nm; (◐) CuCl, 433.4 nm; (●) CuI, 249.2 nm.

Fig. 3. Excitation temperature of copper atoms and β-value calculated. Flow rate of hydrogen: (◐) 6 l min⁻¹, (●) 9 l min⁻¹, (○) 12 l min⁻¹; air, 3 l min⁻¹ throughout.

2-3-2 Inter-element effect between iron and chromium in an air-acetylene flame

Air—acetylene flames are probably employed more frequently for atomization than any of the other possible modes available for atomic absorption spectrometry (a.a.s.). In practical analyses by flame a.a.s., many interferences arise from inter-element effects attributable to chemical reactions in flames rather than from changes in temperature and/or ionization of atoms. Many approaches to the problems of chemical interferences have been reported [98–102]. Most of the mechanisms proposed have been deduced from observations of the changes in atomic absorption responses. An alternative approach should assist in better clarification of the atomization processes.

In this section the determination of the β values for the reactions CrO → Cr + O and FeO → Fe + O in an air–acetylene flame is described and the results are applied to elucidation of the inter-element effect in the flame emission and atomic absorption sepctrometry of chromium and iron. As described previously, the excitation temperature was established by comparing two atomic emission lines with different upper-level energies (the

so-called two-line method). After the excitation temperature had been determined, the β value was estimated by comparing an atomic emission line and a molecular emission line of the diatomic metal oxide. This technique has the advantage that it requires no assumptions about reaction equilibria.

Basic formulae and emission lines observed

The emission lines observed for the oxides of chromium and iron depend on the vibrational structure (0—0 transition). For this case, the degree of atomization β in the dissociation reaction of oxide MO → M + O is given by

$$\beta = \left\{1 + \frac{p(\lambda_M)R_{MO}\lambda_{MO}q_{e,MO}(T_{e,MO})q_{v,MO}(T_{v,MO})g_M A_M}{p(\lambda_{MO})R_M\lambda_M q_{e,M}(T_{e,M})g_{MO}A_{MO}} \exp\left(\frac{E_{MO}}{kT_{e,MO}} - \frac{E_M}{kT_{e,M}}\right)\right\}^{-1} \quad (1)$$

where $p(\lambda_M)$ and $p(\lambda_{MO})$ are response factors which are products of the sensitivity curve of the photomultiplier tube and the reflection efficiency of the monochromator grating, R_{MO} and R_M represent the instrumental responses, λ_{MO} and λ_M the wavelengths, $q_{e,MO}(T_{e,MO})$ and $q_{e,M}(T_{e,M})$ the electronic partition functions, $q_{v,MO}(T_{v,MO})$ the vibrational partition function, g_{MO} and g_M the statistical weights, A_{MO} and A_M the transition probabilities for spontaneous emission, E_{MO} and E_M the upper-level energies, $T_{e,MO}$ and $T_{e,M}$ the excitation temperatures, $T_{v,MO}$ the vibrational temperature and k the Boltzmann constant; subscripts M and MO indicate the atom M and the MO molecule, respectively. The vibrational partition function is given by

$$q_{v,MO} = \{1 - \exp(h\nu_{MO,v}/kT_{v,MO})\}^{-1} \quad (2)$$

where $\nu_{MO,v}$ is the frequency of the first fundamental vibration of the diatomic metal oxide. The electronic partition functions (de Galan et al.[92]) are given by

$$q_{e,MO} = \sum_j g_{MO,j} \exp(-E_{MO,j}/kT_{e,MO}) \quad (3)$$

$$q_{e,M} = \sum_i g_{M,i} \exp(-E_{M,i}/kT_{e,M}) = \sum_{m=1} a_m (T/1000)^{m-1} \quad (4)$$

It seems reasonable to assume that there are thermal equilibria among the various (translational, rotational, vibrational and electronic) energy systems of different species in chemical flames. Thus the following equation is obtained

$$\beta = \left\{1 + \frac{p(\lambda_M)R_{MO}\lambda_{MO}q_{e,MO}(T_{e,M})q_{v,MO}(T_{e,M})g_M A_M}{p(\lambda_{MO})R_M\lambda_M q_{e,M}(T_{e,M})g_{MO}A_{MO}} \exp\left(\frac{E_{MO} - E_M}{kT_{e,M}}\right)\right\}^{-1} \quad (5)$$

The excitation temperature of atoms $T_{e,M}$ is given by the expression

$$T_{e,M} = (E_{M,2} - E_{M,1})/\ln\left\{\frac{p(\lambda_{M,2})R_{M,1}\lambda_{M,1}g_{M,2}A_{M,2}}{p(\lambda_{M,1})R_{M,2}\lambda_{M,2}g_{M,1}A_{M,1}}\right\} \quad (6)$$

where the subscripts 1 and 2 indicate the atomic lines with different upper energy levels.

Thus, if the instrumental responses to the two atomic and one molecular

line emissions are known, the excitation temperature and degree of atomization can be estimated. Once they have been estimated, the relative number of atoms and molecules, and the relative total number of atoms and molecules, can be established. In inter-element effects, the latter parameter is a measure of the contribution of other reactions to the single reaction of oxide dissociation. These three parameters can be expressed by the following relations, respectively

$$N_M \propto \beta N_{MO+M} \tag{7}$$

$$N_{MO} \propto (1 + \beta) N_{MO+M} \tag{8}$$

$$N_{MO+M} \propto \frac{R_M hc q_{e,M}(T_{e,M})}{p(\lambda_M)\lambda_M \beta g_M A_M} \exp(E_M/kT_{e,M}) \tag{9}$$

$$\propto \frac{R_{MO} hc q_{v,MO}(T_{e,M}) q_{e,MO}(T_{e,M})}{p(\lambda_{MO})\lambda_{MO}(1-\beta) g_{MO} A_{MO}} \exp(E_{MO}/kT_{e,M}) \tag{10}$$

where h is the Planck's constant and c the velocity of light. Expression (9) is suitable for large β values while relation (10) is valid for small values.

The atomic and molecular emission lines observed and their physical properties are listed in Table 2.

Apparatus

The atomic absorption/flame emission spectrometer used was a Techtron Model AA-4 fitted with a Techtron slit burner, a photomultiplier tube (HTV R666S), a Sanei Sokki Visigraph (recording) oscillograph and a Hitachi QPD-33 chart recorder. A horizontal slit of 2 mm width was located in front of the entrance slit of the spectrometer, so that a small section in the flame could be observed. Both the entrance and exit slit widths were 50 μm. In order to tune the emission from the flame to the frequency of the phase-selective amplifier of the spectrometer, a Techtron mechanical chopper synchronized at 285 Hz was located between the burner and the spectrometer. The slot burner was turned 90° from the normal position to avoid self-absorption.

Fuel-rich and lean air—acetylene flames were employed in examining the behavior of the species of interest. The flow rates of air and acetylene were 6 l min^{-1} and 1—1.6 l min^{-1}, respectively.

Reagents

A standard stock solution (20 mmol l^{-1}) of chromium(VI) was prepared

TABLE 2

Emission lines observed and their parameters

Line	Wavelength (nm)	Energy (cm^{-1})	gA (10^8 s^{-1})	Response factor p
Cr I	357.9	0—27935	8.3	21.8
Cr I	429.0	0—23305	0.95	10.6
CrO	605.2	0—16595	0.18[a]	1.0
Fe I	349.1	416—29056	0.58	19.0
Fe I	372.0	0—26875	2.5	19.3
FeO	579.0	0—17293	0.16[a]	1.2

[a]Calculated value; other values from C. H. Corliss et al. [93].

by dissolving potassium dichromate in distilled, deionized water. A standard stock solution (20 mmol l^{-1}) of chromium(III) was prepared by evaporating an aliquot of the standard stock chromium(VI) solution almost to dryness with hydrochloric acid, and diluting with distilled, deionized water. For the standard stock solution (80 mmol l^{-1}) of iron(III), electrolytically deposited iron was dissolved in a minimum amount of hydrochloric acid and oxidized with nitric acid by evaporation almost to dryness, before appropriate dilution. The acidity of the chromium(III) and iron(III) solutions was adjusted to 0.1 M with hydrochloric acid.

Dependence of the instrumental response on the wavelength

In order to determine the response factor $p(\lambda)$, the dependence of the instrumental response on the wavelength was measured by using the continuum radiation from a tungsten lamp. The temperature of the lamp filament was measured with an optical pyrometer (Hokushin Electric Co.). The theoretical curve of the dependence of the continuum emission intensity on the wavelength was calculated by the Planck equation. The response factor was defined as the instrumental response divided by the theoretical value.

Emission spectra of CrO and FeO

Figure 4 and 5 show the emission spectra of CrO [9] and FeO [103], respectively. They also include background emission bands from C_2. The 'line' arising from the transition between the vibrational levels $v' = 0 \rightarrow v'' = 0$ was employed to estimate the β-value. This line consists of many rotational transitions, which cause line broadening. It is therefore necessary to integrate the emission peak to determine the net intensity. The ratio of the peak intensity to the integrated intensity was determined beforehand, and the peak intensity measured was calibrated with this ratio.

In previous section, the CuCl emissions in an air–hydrogen flame were given. In the air–acetylene flames, however, no CrCl or FeCl emission peaks were detected when chromium (III) chloride or iron (III) chloride

Fig. 4. Typical emission spectrum of CrO displayed on the oscillograph.

Fig. 5. Typical emission spectrum of FeO displayed on the oscillograph.

solutions were sprayed, and there was no significant difference in the spectra of the chromium (III) chloride and dichromate solutions. This suggests that in the air–acetylene flames any chloride species are atomized and/or oxidized. Accordingly, by monitoring the behavior of the oxides, the atomization process of chromium and iron in the air–acetylene flame can be characterized.

6

Profiles of extremely fuel-rich and lean flames and atomization behavior

In order to characterize the flame and atomization processes, two very different flame compositions were used. The fuel-rich flame gave the usual strong yellow emission from C_2 and carbon particles. Figure 3 shows the distribution of the atomic and molecular emissions at different heights in the flame above the burner top. The intensities are corrected by the instrumental response factor. It can be seen that in the fuel-rich flame all the emissions are increased and there are no significant differences in emission distribution between Cr(III) and Cr(VI). However, since the emission intensity is a function of many changeable parameters such as the excitation temperature, the degree of atomization and the total number of species, as discussed above, it is these parameters that should be monitored rather than the emission intensity.

Figure 7 shows the distribution of the excitation temperature of chromium atoms with height in the flame. Incomplete combustion causes the temperature of the fuel-rich flame to be lower than that of the fuel-lean flame. If it was only the thermal energy that contributed to the degree of atomization and excitation, the higher temperature of the fuel-lean flame should give the more intense emissions. However, Fig. 3 indicates that the chromium and

Fig. 6. Intensity distribution of the atomic and molecular emission lines in the air–acetylene flames. Broken and solid lines indicate the fuel-rich and lean flames, respectively. Solutions: (○) Cr(III); (◐) Cr(VI); (●) Fe. Lines: CrO 605.2 nm for 1, 2 and 3; Cr I 429.0 nm for 6, 10 and 11; Cr I 357.9 nm for 7, 12 and 13; FeO 579.0 nm for 4 and 5; Fe I 372.0 nm for 8 and 9; Fe I 349.1 nm for 14 and 15. The intensities of Fe I and FeO lines are divided by the molar concentration ratio 20:80.

Fig. 7. Distribution of the excitation temperature for chromium atoms.

iron atom lines are more intense in the fuel-rich flame, which suggests that other factors play an important role in atomization.

Figures 8 and 9 show the distributions of the relative numbers of species and the β values, respectively. The β values for chromium and iron are larger in the fuel-rich flame than in the lean flame; in the lean flame, the β values decrease with increasing height above the burner top, where the temperature is higher. These results emphasize the dominant role of the reducing atmosphere in the atomization of chromium and iron in the air—acetylene flame, for the reducing power is greater in the lower region of the flame where the β values are largest. The β values for iron are somewhat smaller than those for chromium in both flames, probably because of the difference in the dissociation energy D_0. The reported dissociation energies of FeO and CrO are 4.8 and 3.8 eV, respectively [104]. There is no significant difference in the β values of Cr(III) and Cr(VI) solutions sprayed into the fuel-rich flame, whereas the β value for Cr(VI) is somewhat smaller than that of Cr(III) in the lean flame. This suggests that there is a certain difference in, for example, the activity or excited state of CrO resulting from $K_2Cr_2O_7$ and $CrCl_3$.

Fig. 8. Distribution of the relative number of species in fuel-rich and lean flames. The relative numbers of iron species are divided by the molar concentration ratio 20:80. (○) Cr(III); (◑) Cr(VI); (●) Fe(III).

Fig. 9. Distribution of the β values. (○) Cr(III); (◑) Cr(VI); (●) Fe(III).

All species are increased in relative number in the fuel-rich flame (Fig. 8). As described above, the total number of atoms and diatomic molecules, N_{M+MO}, provides a measure for estimating the contribution of species other than the diatomic oxides to the atomization process. Both N_{Cr+CrO} and N_{Fe+FeO} are enhanced in the fuel-rich flame, probably because of increased

reduction of polyoxides from the sample to the monoxide compared with the fuel-lean flame. Despite the smaller dissociation energy of the CrO bond, N_{Cr+CrO} is smaller than N_{Fe+FeO} in both flames. This is partly because Cr_2O_3, which is the polyoxide most likely to be present at temperatures above 1600°C, is more stable than the polyoxides Fe_2O_3 and Fe_3O_4.

Inter-element effects on the flame emission/atomic absorption of chromium and iron

This method was applied to elucidation of the inter-element effects on the flame emission/atomic absorption of chromium and iron. Figure 10 shows the inter-element effects. In the emission of chromium, a depressive effect is

Fig. 10. Inter-element effects on Cr I and Fe I emission intensity for fuel-rich (- - -) and lean (——) flames.

found between Cr(III) and Fe(III) in the fuel-rich flame, and between Cr(III) or Cr(VI) and Fe(III) in the fuel-lean flame. There is a slightly enhancing effect in the emission of chromium between Cr(VI) and Fe(III) at the lowest position of the fuel-rich flame and concealed in the tail region of the flame. A depressive effect is found in the emission of iron in the presence of Cr(VI) in the fuel-rich flame, and a slightly enhancing effect with both Cr(III) and Cr(VI) present, in the tail region of the fuel-lean flame. Similar effects have been reported for the atomic absorption spectrometry of chromium and iron [105].

To examine the mechanisms of the inter-element effects, the dependence of the relative numbers of atoms, the β values and the relative total numbers of atoms and diatomic oxide on the height above the burner top was studied (Figs. 11–13). It can be seen that in the lower region of the fuel-rich flame, chromium atoms resulting from Cr(III) decrease in relative number when Fe(III) is present whereas those from Cr(VI) solution increase slightly. This effect disappears in the tail region of the flame. In the fuel-lean flame, the relative number of chromium atoms is depressed by the presence of Fe(III) for both Cr(III) and Cr(VI). Similar changes occur in the β values and the

relative total numbers of atoms and monoxides (Figs. 12 and 13). The changes in the β values for iron and in the relative total number of atoms and monoxides, are clear from Figs. 12 and 13. These pronounced effects indicate the following mechanisms. The selective and mutually depressive effect between Cr(III) and Fe(III) found in the fuel-rich flame can be attributed chiefly to

Fig. 11. Effects of the presence of co-existing element on the relative number of atoms.

Fig. 12. Effects of the presence of co-existing element on the β value.

the formation of refractory mixed polyoxides, but partly also to a decrease in the dissociation of monoxides to atoms. The most likely forms of the mixed polyoxide are $FeO \cdot Cr_2O_3$ and $CrO \cdot Fe_2O_3$. The slight increase in the β value of CrO and decrease in that of FeO between Cr(VI) and Fe(III) in the fuel-rich flame is probably due to transfer of the oxygen atom from CrO to Fe; the dissociation energy of FeO is larger than that of CrO (see above).

In the lean flame, decreases in the β value and the total number of atoms and diatomic oxides of chromium again occur and this is not specific to Cr(III) or Cr(VI). Since the decreases in the β values of CrO and FeO take

Fig. 13. Effects of the presence of co-existing element on the relative total number of atoms and diatomic oxide.

place concurrently, they cannot be attributed to the oxygen transfer reaction. A possible mechanism is the mutual promotion of oxidation of atoms by a catalytic action of the monoxides and/or polyoxides. At higher positions in the flame, the decomposition of the mixed metal polyoxide decreases.

It is difficult to explain why the mixed oxide formation and oxygen transfer reactions should be specific to Cr(III) and Cr(VI), respectively. Differences in activity between atoms and/or monoxides resulting from Cr(III) and Cr(VI) salts are probable: from $CrCl_3$ chromium atoms are produced first and then oxides are formed, whereas from dichromate, this order is reversed. Thus a difference in the change of the excited state would be expected when Fe(III) is present. In practice, the excitation temperature of chromium atoms resulting from Cr(VI) was higher than that from Cr(III) by −75 to 175 K (depending on the position) in the fuel-rich flame when Fe(III) was present in the solution; the difference in the lean flame was smaller. In contrast, the excitation temperature of iron atoms was enhanced by the presence of Cr(III) but unchanged by Cr(VI) in the fuel-rich flame. This again indicates that energy transfer occurs differently from the different species resulting from Cr(III) or Cr(VI).

The approach seems to be applicable to studies of inter-element effects between chromium and elements other than iron. Inter-element effects on atomic absorption between chromium and other elements have been classified [105] into three categories; (a) enhancing effects by Cu, Ba, Al, Mg and Ca; (b) depressive effects by Sr, Na, K, Zn and Sn, which were pronounced in the lower region of the flame; (c) a selective effect by iron. The first may be attributed to transfer of the oxygen atom, and the second to mixed oxide formation and catalytic action on the oxidation reaction. For example, the dissociation energy of CuO (4.5 eV) is larger than that of CrO (3.8 eV) [104], so that oxygen can be transferred to copper. The effect by iron appears to include all these reactions.

2-4 Application to Electrothermal Atomizers

In the previous section, the multi-line method is applied to the elucidation of the atomization processes or inter-element effect in the chemical flame atomizer. Electrothermal atomizers are also commercially available and recently used in the practical analysis by AAS. With the pervasion of the electrothermal atomizers, there have arised problems associated with complicated atomization processes and inter-element effects. Up to date, few systematic approach to the mechanisms has been reported. In this section, systematic analysis of the mechanisms by means of the four-line method is described. In the electrothermal atomizers, the atomic emission was very weak for the line of high excitation energy. Therefore, the excitation temperature was determined by atomic absorption. In Sec. 2-4-1, basic aspects of the two-line method by atomic absorption for determinig the excitation temperature are described. In Sec. 2-4-2, this method is combined with the multi-line method for estimating the atomization process in an electrically heated glassy carbon tube atomizer.

2-4-1 Measurement of excitation temperature by atomic absorption

Temperature determination is the basis of evaluating diverse properties associated with atomic absorption spectrometry, such as the degree of dissociation, atomic population and so on. Winefordner [106] reported a two-line method for atomic absorption of In, Ga or Tl, but no worker has published a paper concerning the measurement of temperature directly above the surface of electrothermal atomizer by means of the maximum absorbance comparison method.

In this section, a method is described for the measurement of the excitation temperature, utilizing a resonance line and doublet lines of lead which have different lower energies. Atomic excitation temperature above strip type electrothermal atomizers (tantalum or glassy carbon strip [107, 108]) is examined in an argon atmosphere. It is also shown that the excitation temperature in analytical flame can be determined quickly with this method.

Theory

If the current for a hollow cathode lamp is small enough for one component of the doublet lines not to be absorbed by the other and the spectral band-pass width of a monochromator is wide enough to pass them through, the apparent absorbance for the doublet can be expressed as

$$A=\ln[(I_1^0+I_2^0)/(I_1+I_2)], \tag{1}$$

where I_1^0, I_2^0 and I_1, I_2 are the intensity of the incident and the transmitted light, respectively. Subscripts 1 and 2 stand for the components 1 and 2 of the doublet, respectively.

The intensity of the incident light, I_1^0 and I_2^0 are written as

$$I_2^0=[(g_2f_2\lambda_1^3)/(g_1f_1\lambda_2^3)]I_1^0 \exp[(E_{1u}-E_{2u})/(kT_u)], \tag{2}$$

where g_1 and g_2, f_1 and f_2, λ_1 and λ_2, and E_{1h} and E_{2h} are the statistical weight, the oscillator strength, the wavelength, the upper state energy for the doublet lines, respectively, k is the Boltzmann constant and T_H is the excitation temperature in the hollow cathode lamp.

Since $E_{1h} - E_{2h}$ is small and T_H is high, the factor $\exp[(E_{1h} - E_{2h})/kT_H]$ in Eq. (2) can be replaced by unity; i.e.,

$$I_2^0 \doteqdot \frac{g_2 f_2 \lambda_1^3}{g_1 f_1 \lambda_2^3} I_1^0. \tag{3}$$

The intensity of the transmitted light, I_1 and I_2 may be expressed as

$$I_1 = I_1^0 \exp(-K_{1,\max} l)$$

and

$$I_2 = I_2^0 \exp(-K_{2,\max} l),$$

where $K_{1,\max}$ and $K_{2,\max}$ are maximum absorbances for the doublet lines and l is the thickness of the absorbing layer. Then, Eq. (1) becomes

$$e^A = \left(1 + \frac{g_2 f_2 \lambda_1^3}{g_1 f_1 \lambda_2^3}\right) \Big/ \left[\exp(-K_{1,\max} l) + \frac{g_2 f_2 \lambda_1^3}{g_1 f_1 \lambda_2^3} \exp(-K_{2,\max} l)\right]. \tag{4}$$

We have

$$\Delta\nu_D = 2\sqrt{\frac{2R \ln 2}{c}}\, \nu_0 \sqrt{\frac{T}{M}}, \tag{5}$$

where $\Delta\nu_D$, R, c, T, and M are the Doppler width, the gas constant, the light velocity, the translational temperature of gas and the molecular weight, respectively.

When, on the other hand, the doppler broadening alone is present, the maximum absorption coefficient, K_0, can be calculated by

$$K_0 = \frac{2}{\Delta\nu_D} \sqrt{\frac{\ln 2}{\pi}}\, \frac{\pi e^2}{mc} Nf, \tag{6}$$

where $N = [N_0 g/Q(T)] \exp(-E/KT)$ and $Q(T)$ is the partition function of atom.

When Eq. (5) is substituted into Eq. (6), K_0 becomes

$$K_0 = \frac{\pi e^2}{mc} \sqrt{\frac{M}{2\pi RT}}\, \frac{N_0 g f \lambda_0}{Q(T)} \exp\left(\frac{-E}{kT}\right). \tag{7}$$

Using Eq. (7), we have

$$\frac{K_{1,\max} l}{K_{R,\max} l} = \frac{g_1 f_1 \lambda_1}{g_R f_R \lambda_R} \exp\left(\frac{E_{1,R} - E_{1,1}}{kT}\right), \tag{8}$$

$$\frac{K_{2,\max} l}{K_{R,\max} l} = \frac{g_2 f_2 \lambda_2}{g_R f_R \lambda_R} \exp\left(\frac{E_{1,R} - E_{1,2}}{kT}\right), \tag{9}$$

where the subscripts L and R stand for the lower energy level and resonance line, respectively. Since $E_{LR}=0$ and $K_{R.max}\ l=A_R$, Eqs. (8) and (9) are written as

$$K_{1.max}\,l=A_R\frac{g_1f_1\lambda_1}{g_Rf_R\lambda_R}\exp\left(\frac{-E_{L1}}{kT}\right), \tag{10}$$

$$K_{2.max}\,l=A_R\frac{g_2f_2\lambda_2}{g_Rf_R\lambda_R}\exp\left(\frac{-E_{L2}}{kT}\right). \tag{11}$$

Substituting Eqs. (10) and (11) into Eq. (4), we obtain

$$\exp\left[-A_R\frac{g_1f_1\lambda_1}{g_Rf_R\lambda_R}\exp\left(-\frac{E_{L1}}{kT}\right)\right]+\frac{g_2f_2\lambda_1^3}{g_1f_1\lambda_2^3}\exp\left[-A_R\frac{g_2f_2\lambda_2}{g_Rf_R\lambda_R}\exp\left(\frac{-E_{L2}}{kT}\right)\right]$$
$$-\left(1+\frac{g_2f_2\lambda_1^3}{g_1f_1\lambda_2^3}\right)\exp(-A)=0. \tag{12}$$

Table 1. Physical properties of lead [109].

Lines		Wavelength (nm)	gf-values	Energy Levels (eV)
Resonance line (A_R)		283.3	0.22	0—4.375
Doublet lines (A)	1	261.37	0.19	0.969—5.711
	2	261.42	2.7	0.969—5.712

As for the Pb 1 lines in Table 1, Eq. (12) can be written as

$$\begin{aligned}&\exp[-0.797A_R\exp(-11240/T)]\\&+14.21\exp[-11.32A_R\exp(-11240/T)]\\&-15.21\exp(-A)=0.\end{aligned} \tag{13}$$

If A and A_R are provided as data, T can be computed with trial-and-error calculation by a computer.

Apparatus A Nippon Jarrell-Ash AA-1 E atomic absorption and atomic emission spectrometer fitted with a strip type electrothermal atomizer was used. The radiation from a hollow cathode lamp of lead (current of 7 mA) was focused right above the center of the atomizer through a lens and a tantalum slit (0.5 mm dia.) A Hitachi Model QPD-54 recorder was employed. The atomizer system was designed to allow the strip to move over a range of 15 mm.

Reagents Standard lead solutions of 1 mg/m*l* were prepared by dissolving pure metal in a minimum amout of nitric acid and diluted just before using them.

Procedure Aliquots of 4 ng (2 ppm, 2 μl) and 10 μg (5000 ppm, 2 μl) were taken for the measurements of the resonance line and the doublet, respectively, on the depression of the strip using a 5 μl syringe (S.G.E., PTY., Co., Australia). The atmosphere in the chamber was purged by a regulated stream of argon gas (2.1 l/min.). Evapolation of the solvent was carried out at a low temperature (ca. 100~200°C), and followed by atomization at higher tem-

perature. All atomic absorption signals were recorded as a peak and the absorbance was calculated from the peak height. The temperature on the surface of the strip was measured with an optical pyrometer which was corrected for spectral emissivities, 0.3 for tantalum and 0.8 for glassy carbon strips.

Excitation Temperature above the strip type electrothermal atomizers

Figure 1 shows the results of temperature measurements for two kinds of atomizers. Temperature measurements were carried out using the beam of about 1 mm diameter in the range of a few millimeters above the atomizer. The absorbance for the doublet lines was observed to be much lower value compared with that for the resonance line, but a linear relationship between the absorbance and the concentration was obtained in the range of 0 to 10 μg. As is seen in Fig. 2 the observed excitation temperature of lead increases monotonically as the set temperature of the glassy carbon strip increases. However, the increment of the excitation temperature decreases for higher final temperatures, suggesting that atomization of lead must have ended before the final temperature is attained partly because there exists a remarkable leading time for the strip to reach the equilibrium final tempera-

ig. 1. Excitation temperature of lead measured above a tantalum (at 2000 K) and a glassy carbon (at 1800 K) strip atomizer.
A: Tantalum strip, B: Glassy carbon strip, Flow rate of argon: 2.1 *l*/min.

Fig. 2. Excitation temperature of lead vs final temperature of a glassy carbon strip. Flow rate of argon: 2.1 *l*/min., Height of the beam above the glassy carbon strip: 0.5 mm.

Fig. 3. Excitation temperature in air-acetylene flame measured by the present method as a function of the flow rate of acetylene. Height of the beam above the burner top: 5.5 mm, Diameter of the beam: 3.0 mm.

ture. Furthermore, oscilloscopic measurements of the transient temperature change also revealed that the atomization of lead was completed at much lower temperature than the finally attained temperature of the strip. For example, the atomization of lead started at 1000 K and finished at 1200 K, showing a maximum at 1100 K when the final temperature was set at 1800 K.

Excitation temperature in air-acetylene flame

The present method is also applicable to rapid determination of excitation temperatures in analytical flame, simply measuring the absorbance of characteristic lead lines. Figure 3 shows variation of the temperature at 5.5 mm above the burner top as a function of the acetylene flow rate under the constant air flow rate. Figure 4 shows the temperature variations as a function of height above the burner top. The precision of the measurement obtained was about 7%, mainly due to sampling error for the electrothermal atomization and less than 2% for the flame.

The present method is promising for estimating relatively low temperature in electrothermal atomizers, that seems to be difficult to measure by emission method, and is applicable to elements, such as nickel containing a pair of absorption lines having different lower levels. The excitation temperature in flame can easily be measure by this method.

Fig. 4. Excitation temperature in air-acetylene flames measured by the present method as a function of the height above the burner top. Flow rate of acetylene: 2.1 *l*/min (A), 1.8 *l*/min (B). Diameter of the beam: 3.0 mm.

2-4-2 Atomization processes in a glassy carbon tube atomizer

As the importance of the electrothermal atomizer becomes greater in practical analysis for trace amounts of elements by atomic absorption spectrometry, it is necessary to elucidate the mechanisms of the atomization process. Interference effects by matrices and changes in absorption with the form of the salt are often encountered in routine analysis. As well as the

loss of the element as non-atomic species, these effects seem to be critical factors in causing poor accuracy and precision. The degree of atomization β is one of the indicative parameters for these effects. Many approaches for determining the β value have been reported [110–112]. These methods have been applied mainly to chemical flames. It appears to be difficult to apply them to electrothermal atomizers because they are not based on the determination of the β value in a unit reaction and there is no accepted standard for comparison.

In a previous section, an alternative method was briefly described for the determination of the β value in the reaction CuCl → Cu + Cl, and was applied to the atomization of copper(II) chloride in an air–hydrogen flame. An atomic emission line of copper and a molecular emission line of CuCl (0,0) were compared. This method has the advantage that equilibrium of the chemical reactions is not required.

In this section, an application of this method is described for the determination of the β value in the reaction CuCl → Cu + Cl in a glassy-carbon tube atomizer, and the effect of trace hydrogen mixed with the argon carrier gas on the atomization is discussed.

The expressions used here are the same as those used in Sec. 2-3-1. A ratio of the atomic and molecular emission is given by:

$$p(\lambda)\frac{R_{Cu}}{R_{CuCl}} = \frac{\beta\lambda_{CuCl}q_{CuCl,e}(T_{CuCl,e})\,q_{CuCl,v}(T_{CuCl,v})\,g_{Cu}A_{Cu}}{(1-\beta)\lambda_{Cu}Q_{Cu}(T_{Cu})A_{CuCl}}\exp\left(\frac{E_{CuCl}}{kT_{CuCl,e}} - \frac{E_{Cu}}{kT_{Cu}}\right) \quad (14)$$

where λ is the wavelength and $p(\lambda)$ the instrumental response factor which is a product of the quantum yield of the photocathode and the reflection efficiency of the grating. These factors vary with the wavelength. Except for such a case as a plasma at a reduced pressure, it can be reasonably assumed that the temperatures of different systems are approximately the same or the systems are in quasi thermal equilibrium. Therefore, with the approximation $T_{CuCl,e} \simeq T_{CuCl,v} \simeq T_{Cu}$, the degree of atomization is given by:

$$\beta = \left\{1 + \frac{R_{CuCl}\lambda_{CuCl}q_{CuCl,e}(T_{Cu})q_{CuCl,v}(T_a)g_{Cu}A_{Cu}}{p(\lambda)R_{Cu}\lambda_{Cu}Q_{Cu}(T_{Cu})A_{CuCl}}\exp\left(\frac{E_{CuCl}-E_{Cu}}{kT_{Cu}}\right)\right\}^{-1} \quad (15)$$

The excitation temperature was determined by a two-line method of atomic absorption. Although the aim was to measure the excitation temperature of copper, a suitable pair of copper lines was not available, so that other elements (Pb, Sn and Ni) were used for the temperature measurement with the assumption described above that their excitation temperatures were the same.

Browner and Winefordner [113] reported a two-line atomic absorption method based on indium, gallium and thallium for temperature measurement with a quartz iodine continuum radiation source. This method does not involve large errors in absorbance and is not greatly affected by changes in absorption line profile. However, the low sensitivity seems to restrict its application to special cases.

An alternative two-line method based on maximum atomic absorption of lead with the use of a conventional line source (hollow-cathode lamp) has already been reported; the method was applied to the measurement of the

excitation temperature of lead atoms above a glassy carbon strip atomizer. This method has the advantage of high sensitivity but concurrently the disadvantage that the absorption line profile is a critical factor for the precision of the temperature measurement. In the previous section, the Doppler broadening of the absorption line was taken into account. In the present paper, the contribution of Lorentz broadening to the error is discussed.

When Doppler and Lorentz broadening are present and the natural broadening is negligibly small, the absorption coefficient is given [114] by

$$k_\nu = k_0 \frac{a'}{\pi} P(\omega, a'),$$

where $P(\omega,a') = \int_{-\infty}^{\infty} e^{-y^2}/[a'^2 + (\omega - y)^2]\,dy$, $\omega = 2(\nu - \nu_0)(\ln 2)^{1/2}/\Delta\nu_D$, $y = 2\,\delta(\ln 2)^{1/2}/\nu_D$, and $a' = \Delta\nu_L(\ln 2)^{1/2}/\Delta\nu_D$. Also

$$k_0 = \frac{2}{\Delta\nu_D}\left(\frac{\ln 2}{\pi}\right)^{1/2} \frac{\pi e^2}{mc} Nf \tag{16}$$

$$\Delta\nu_D = 2\left(\frac{2R \ln 2}{c}\right)^{1/2} \nu_0 \left(\frac{T'}{\mu}\right)^{1/2} \tag{17}$$

$$\Delta\nu_L = 2\left(\frac{2}{\pi}\right)^{1/2} N' \left(\frac{RT'}{\mu}\right)^{1/2} \left(\frac{\sigma + \sigma'}{2}\right) \tag{18}$$

where ν is the wavenumber, ν_0 the wavenumber at the center of the absorption line, $\Delta\nu_D$ the Doppler width, δ the variable of integration, k_0 the maximum absorption coefficient when Doppler broadening alone is present, e the charge on the electron, m the mass of the electron, c the velocity of light, N the concentration of atoms whose electron is in the lower transition level, f the oscillator strength, T' the translational temperature or gas temperature, R the gas constant, $\Delta\nu_L$ the Lorentz broadening, μ the reduced atomic or molecular weight of the colliding system, N' the concentration of the foreign species, and σ and σ' the diameters of the colliding species. The maximum absorption coefficient is given by

$$k_{\nu,\max} = k_0 a' \pi^{-1} P_{\max}(a')$$

Where the Boltzmann law applies, the concentration N can be replaced by $N = N_t\beta(1 - \chi)g_L \exp(-E_L/kT_a)/Q_a(T_a)$, where N_t is the total number of molecular, atomic and ionic species containing the element of interest, χ the degree of ionization, g_L the statistical weight of the lower level and E_L the energy level of the lower level. Letting $U_{\max}(a') = k_{\nu,\max}/k_0$ and taking a ratio of absorbance for two atomic lines with different lower level energy gives

$$\frac{A_{1,\max}}{A_{2,\max}} = \frac{k_{\nu,1,\max}}{k_{\nu,2,\max}} = \frac{k_{0,1}}{k_{0,2}} \frac{U_{\max}(a_1')}{U_{\max}(a_2')}$$

Substituting eqns. (16) and (17) gives

$$\frac{A_{1,\max}}{A_{2,\max}} = \frac{\lambda_2 f_1 g_{L,1} U_{\max}(a_1')}{\lambda_1 f_2 g_{L,2} U_{\max}(a_2')} \exp\{(E_{L,2} - E_{L,1})/kT_a\}. \tag{19}$$

For small difference in a' values, the following equation can be employed:

$$U_{\max}(a_1') = U_{\max}(a_2')\left\{\left(\frac{dU_{\max}}{da'}\right)_{a' = a_2'} (a_1' - a_2') + 1\right\}.$$

Equations (3) and (4) give

$a' = [0.5(\sigma + \sigma')]^2 \lambda \pi^{-1/2}$

Therefore, $a'_1 - a'_2 = a'_1(1 - a'_2/a'_1) = a'_1(1 - \lambda_1/\lambda_2)$.
Consequently, eqn. (5) is replaced by

$$\frac{A_{1,\max}}{A_{2,\max}} = \frac{\lambda_2 f_1 g_{L,1}}{\lambda_1 f_2 g_{L,2}} \left\{1 + \left(\frac{dU_{\max}}{da'}\right)_{a' = a'_2} \left(1 - \frac{\lambda_1}{\lambda_2}\right)\right\} \exp\ \{(E_{L,2} - E_{L,1})/kT_a\} \quad (20)$$

Thus, the ratio of wavelengths is a variable yielding the variation of absorbance. The first ratio of wavelengths originates from the Doppler width and the second one (in parentheses) from the Lorentz broadening. When $A_{1,\max}/A_{2,\max}$ is found experimentally, the excitation temperature T_a can be calculated from eqn. (20).

Once the excitation temperature has been determined, the degree of atomization β can be estimated from eqn. (15) from the emission intensities of copper atoms and CuCl molecules, R_{Cu} and R_{CuCl}.

Table 2 lists parameters for the two lines of the three elements lead, tin and nickel. The equations for calculating the excitation temperature do not include the term attributed to the Lorentz broadening or the term in the first braces in eqn. (20). The effect of this term will be discussed for nickel, which was selected for the determination of the excitation temperature.

Apparatus and reagents

The components used are listed in Table 3. A glassy carbon tube (2 mm i.d., 3 mm o.d. and 30 mm long; Tokai Carbon Co. Ltd.) was fitted to stainless steel electrodes through cubic graphite mounts which served as thermal

TABLE 2

Elements and equations used for the determination of excitation temperature

Element	Wavelength (nm)	Energy (cm^{-1})	gf value[a]	B.p. (°C)
Pb	λ_1 283.3	0—35287	0.22	1750
	λ_2 261.4 {261.365	7819—46069	0.19	
	261.418	7819—46061	2.7	
	$\exp\{-0.797A_1 \exp(-11240/T_a)\} + 14.21 \exp\{-11.32A_1 \exp(-11240/T_a)\} - 15.21 \exp(-A_2) = 0$			
Sn	λ_1 270.7	1692—38629	1.1	2275
	λ_2 284.0	3428—38629	2.5	
	$T_a = 2498.6/\{0.8692 + \ln(A_1/A_2)\}$			
Ni	λ_1 352.45	205—28569	0.85	2732
	λ_2 361.9	3410—31031	1.5	
	$T_a = 4616/\{0.595 + \ln(A_1/A_2)\}$			

[a]NBS Monograph 53 (1962).

TABLE 3

Experimental components

Atomic absorption spectrometer	Nippon Jarrell-Ash AA-1
Light source	HTV hollow-cathode lamp
Electrothermal atomizer	Glassy carbon tube located in a glass chamber
Power supply for the electrothermal atomizer	Stepwise transformers
Recorder	Sanei Sokki Co. 5L Visigraph fitted with 6L5 d.c. amplifier

insulators. The glassy carbon tube had an opening (0.8-mm diameter) on the lateral face through which sample solutions were introduced.

Argon was introduced into the atomization chamber at 1.5 l min^{-1}. In order to estimate the reduction power on atomization, hydrogen was premixed with argon.

Stock solutions of copper(II) chloride, lead nitrate, tin(II) chloride, chromium(III) chloride and nickel chloride (all analytical reagent grade) were prepared by dissolution in deionized water; the acidity was adjusted to 1 M. Working solutions were prepared by diluting the stock solution with deionized water and adjusting the acidity to 0.5 M.

Procedures

By a microsyringe (Scientific Glass Engineering Pty.), an aliquot of the sample solution was placed on the bottom of the glassy carbon tube atomizer, dried at 120°C for 2 min and atomized. The amounts introduced are listed in Table 4.

The temperature of the surface of the glassy carbon tube atomizer was measured by an optical pyrometer (Hokushin Electric Co. Ltd.). The transient temperature was determined by tracing the black-body radiation from the atomizer at 550 nm. The resulting photocurrent was calibrated by temperature measurements with the optical pyrometer.

TABLE 4

Amounts of salts introduced into the carbon tube

Salt	Wavelength (nm)	Amount (ng) of element	Salt	Wavelength (nm)	Amount (ng) of element
$CuCl_2$	Cu I 327.4	45×10^3	$SnCl_2$	Sn I 270.7	5
	CuCl 433.3			Sn I 284.0	5
$Pb(NO_3)_2$	Pb I 283.3	0.4	$CrCl_3$	Cr I 357.9	20
	Pb I 284.0	20			
$NiCl_2$	Ni I 352.5	20			
	Ni I 361.9	20			

Excitation temperature

A suitable pair of copper absorption lines with different lower energies could not be found. Therefore, it was necessary to select an alternative element for the determination of the excitation temperature. The excitation temperature was estimated from the absorbances at the absorption peaks of the three elements lead, tin and nickel. Figure 5 shows the relation between the exci-

tation temperatures and the equilibrium temperature of the atomizer surface. It can be pointed out that the excitation temperatures are in the order of the iso-vapor pressure temperature of atoms. This explains the difference in atomization temperature of the three elements.

Figure 6 shows the time correlation for the transient temperature of the atomizer surface, the appearance of the absorption peak and the excitation temperature. The excitation temperatures are in order of the peak appearance and somewhat lower than the temperature of the atomizer surface. Thermal energy may be partly distributed to the atomic system and the remainder to other processes requiring energy such as those involving latent heat or dissociation energy. In addition, the thermal energy can be distributed in the molecular energy system (translational, vibrational or rotational energy) if

Fig. 5. Relation between the excitation temperature and temperature of the atomizer surface.

Fig. 6. Time correlation for the temperature of the atomizer surface, the appearance of the absorption peak and the excitation temperature. (---) Temperature of atomizer surface. T_a is the excitation temperature at peak maximum.

the degree of atomization is not unity. There also is a possibility that, because of the low thermal conductivity between the sample salt and the surface of the atomizer, the transient energy transfer is not enough or the temporal thermal equilibrium between them is incomplete. For these reasons, the excitation temperatures are somewhat lower than the temperature of the atomizer surface. The peak appearance time of nickel is closer to that of copper than are those of lead and tin. Consequently, nickel was chosen as the alternative element for the determination of the excitation temperature.

The error arising from Lorentz broadening is expressed as the term in the first braces in eqn. (20). Figure 7 shows the result of numerical integration of $U_{max}(a')$ by a computer. The value of a' for various elements [115] lies in the range 1—2.5 at 2,000—3,000 K. The value of dU_{max}/da' was determined graphically and found to change from 0.2 to 0.1 over the region of a'. For the pair of nickel lines, the term in the first braces varies from 1.00524 to

1.00655. Thus the Lorentz broadening may cause a maximum error in the absorbance ratio of 1%.

In practice, there arises the Lorentz shift in addition to Lorentz broadening.

Fig. 7. Theoretical curve of the effect of Lorentz broadening on the maximum of an absorption peak. The broken line tangents and arrows indicate a typical region of a'.

Fig. 8. Dependence of the β value for CuCl on the excitation temperature. (○) The experimental curve. Also shown are the theoretical curves at a total pressure of (1) 0.1 atm.; (2) 0.5 atm.; (3) 1 atm.; (4) 2 atm.

No complete theory of a Lorentz-shifted absorption line profile has been proposed except by analogy with emission line profiles [116]. Therefore, it cannot be predicted how much the Lorentz shift contributes to the error. Lenz [116], however, concluded that the magnitude of the Lorentz shift is proportional to that of the Lorentz broadening. According to Lenz's theory, therefore, the Lorentz shift would be $\Delta\nu_S \approx -0.36\Delta\nu_L$ in an argon atmosphere. Taking this into account in the absorbance ratio, it can be suggested that the magnitude of the error does not exceed the error of measurement.

Degree of atomization $\beta(CuCl \rightarrow Cu + Cl)$

It was found that there was a delay between the CuCl and Cu emission peaks of <1 s, which was dependent on the atomizer temperature; the CuCl emission preceded the Cu emission. The time required for achieving the peak copper emission was almost the same as for the nickel absorption. For this reason, the β value was estimated from the data obtained at the time of the peak copper emission. Figure 8 shows the dependence of the β value on the excitation temperature. The theoretical curves were calculated from an assumption of equilibrium in the purely thermal dissociation $CuCl \rightleftharpoons Cu + Cl$ without other chemical reactions, which corresponds to Saha's equation of

thermal ionization. There is a pronounced discrepancy between the experimental and theoretical curves over the possible total pressure range. This suggests that the molecules from the sample are partly reduced. A possible reductant is active carbon from the surface of the glassy carbon atomizer. In a previous study of the diffusion of atoms [117] the adsorption activity of glassy carbon was found to be as weak as that of quartz, compared with graphite. However, the result of the β value indicates that the surface of glassy carbon has a significant reducing power during the atomization of CuCl.

The sample was $CuCl_2$. Therefore, the degree of dissociation β' for the reaction $CuCl_2 \rightarrow CuCl + Cl$ should be evaluated for the determination of the overall degree of atomization $\beta'\beta$. However, it is well known that $CuCl_2$ is completely converted to CuCl above 993°C. Thus, it is fairly reasonable that $\beta = \beta'\beta$.

Effect of hydrogen on the degree of atomization

Figure 9 shows the effect of hydrogen flow rate on the excitation temperature. The temperature of the atomizer surface was 2,100°C when hydrogen was absent. As the flow rate of hydrogen increased, the excitation temperature decreased. This may be attributed to the high thermal conductivity of hydrogen.

Figure 10 shows the effect of the hydrogen flow rate on the degree of atomization. As the flow rate increases, the β value rapidly increases but does not exceed a value of ca. 0.9. This is probably due to the decrease in the temperature of the atomizer surface and partly to the rapid diffusion of CuCl in the hydrogen atmosphere or the short residence time within the hot region in the atomizer. The recommended ratio of flow rates H_2:Ar = 1:300 is enough to double the degree of atomization.

Fig. 9. Dependence of the excitation temperature on the flow rate of hydrogen. The temperature of the atomizer surface was 2373 K.

Fig. 10. Dependence of β value for CuCl on the flow rate of hydrogen at excitation temperatures of (•) 2000 K and (○) 2100 K.

The principal reaction associated with the promotion of atomization may be the abstraction of a chlorine atom by molecular or atomic hydrogen. However, since accurate reaction rates of possible reactions have not been measured, the detailed mechanism cannot be elucidated. If the reaction rates are much larger than the residence time, which is likely in radical reactions at high temperatures, chemical equilibrium applies. In this case, the difference in dis-

sociation energy D_0 may be a means of establishing the principal reaction. Of possible diatomic molecules (CuCl, CCl, CH, H_2, HCl, etc.) HCl has the largest dissociation energy. Therefore, HCl molecules will be most stable in the high temperature environment.

Application to the determination of the β value of $CrCl_3$

The β value determined by the present method can be a standard for the determination of β values of other elements. By comparing the absorbances of copper and chromium, the relative β value was determined. As seen above, the appearance times of the nickel, copper and chromium peak almost coincide. This makes it reasonable to substitute the excitation temperature of nickel for that of copper and chromium, and to estimate the β value of chromium by comparing the copper and chromium absorbances. The relative β value is given by

$$\beta_{Cr} = \beta_{Cu} \frac{A_{Cr}}{A_{Cu}} \frac{\lambda_{Cr} f_{Cu} g_{L,Cu}}{\lambda_{Cu} f_{Cr} g_{L,Cr}} \left[\left(\frac{1}{M_{Ar}} + \frac{1}{M_{Cu}} \right) \Big/ \left(\frac{1}{M_{Ar}} + \frac{1}{M_{Cr}} \right) \right]^{1/2} \frac{Q_{Cr}(T_a)}{Q_{Cu}(T_a)} \frac{W_{Cu} M_{Cr}}{W_{Cr} M_{Cu}} \exp \{(E_{L,Cr} - E_{L,Cu})/kT_a\},$$

where W is the sample weight and the term owing to the Lorentz broadening is neglected. For both resonance lines Cu I 327.40 and Cr I 387.87 nm, the lower term energy is zero. Therefore, the exponential term is simplified to

Fig. 11. Dependence of β value for $CrCl_3$ on the excitation temperature.

unity, Figure 11 shows the dependence of the β value on the excitation temperature. The β value of chromium is somewhat lower than that of copper. If the forward and backward reactions are rapid enough, the difference in β value might be attributable to the difference in dissociation energy D of CuCl and CrCl. The dissociation energy has been reported to be 3.4 and 3.0 eV for CrCl and CuCl, respectively. However, as stated above, a kinetic approach is necessary for clarification of the detailed mechanism.

Application to other elements

The standard β value of CuCl was used to attempt to determine β values for tin(II) chloride and the nitrates of lead and silver. In this application, there is a problem associated with the difference in the appearance time of the peak absorption. If the measurement is timed for the peak maximum of chromium or copper, it coincides with the tail of the silver peak, and is not superimposed

upon any part of the lead or tin peaks. In practice, for example, the β value of silver nitrate was found to be ca. 100% at an excitation temperature of 2,000°C. This value seems likely for the low dissociation energy of AgO, 1.8 eV. However, this value does not coincide with a β value of silver nitrate at the moment of peak maximum of silver absorption. It might, therefore, be best to determine transient β values with the use of a more suitable partner for measuring the standard β value. This comparison method appears to be more useful for the determination of β value of samples atomized in flames where there is no absorption delay.

総　　括
(SUMMARY)

本論文において著者は「痕跡分析のための原子分光法」と題して，それに関る二つの新しい方法，即ち，「原子磁気旋光分光法」と「多線法」について述べた。これらはそれぞれ，原子分光法による分析の際に問題となる二つの大きな障害，即ち (1) 正の誤差を与えるバックグラウンド信号 (2) 正負いずれの誤差をも与える干渉，を除去または補正する方法である。

序論においては，これら二つの現象が目的元素と共存する試料マトリックスが原因となって生ずること，それ故，試料マトリックスの影響を除去するための前処理過程を行わないで直接的に原子化および励起する方法で分析を行う場合には顕著になることを論じた。また，それ以前の問題として，こうした直接分析が必要な背景，即ち，次第に分析試料の量が少なくなりかつマトリックスが複雑になりつつあるということ，を論じた。また，これに関連して，分析化学的な原子分光法（原子分光分析）の歴史的変化および現在の状態をも検討した。無機分析を主体として他の方法との比較を行いそれぞれの特徴と意味を考えた。さらには，その比較の基準となる因子について，無機分析を主体としてではあるが，分析化学という体系の中である程度一般的に考察した。

第1章総括 (Summary of Chapter 1)

こうして，序論において，本論文の主題の意味付け（主題を取り上げた根拠）を述べた後，本論第1章においては「原子磁気旋光分光法」の理論，装置の最適化，応用などについて論じた。その結果，本法には原子けい光分光法に似た以下の特長があることがわかった。

(1) 原子発光分光法のようには原子の熱励起を必要としない。

(2) 原子発光分光法のようには，高い分解能の分散系を必要としない。

(3) 原子吸光分光法のようには，光源光強度の変動が直接的に信号のS／N比に影響しない。

(4) 光源光強度の増加にほぼ比例して信号が増加する，即ち感度が上がる。

それに加えて，次の特長があることもわかった。

(1) 光源光の回収率が原子けい光分光法の場合より高い。したがって，種々の元素について市販されている原子吸光分光法用の中空陰極ランプで十分に実用的感度が得られる。

(2) 原子けい光分光法では問題となるバックグラウンド散乱が除去できる。

(2)の特長は特に試料の直接原子化による分析の際，試料マトリックスから生ずる煙や分子などによるバックグラウンド信号を気にしなくてよいという点で重要な意味がある。直接分析を実際的なものにするために，上記の原子吸光やバックグラウンド吸光による旋光強度の減衰を自動的に補正する光学システムを開発しその最適化を行った。合成試料を使ってその性能を調べた結果90%以上の吸光でも，良い補正が行われることが分った。その後，植物性，動物性および岩石質などの代表的なマトリックスを含む試料について，その中に含まれるいくつかの元素について直接分析を行った。その結果，サンプリング時におけるばらつきなどが主な原因となって精度はあまりよくない（相対

標準偏差が最大で十数％）が，標準試料や研究室間クロスチェックなどから，直接分析にしては満足できる正確さが得られることがわかった。因に，最大相対誤差は分析した種々の試料および元素にわたり，±20％であった。化学的前処理などを含む分析方法では汚染や損失などの問題を考えるとこのような正確さはなかなか得難いものと思われる。原子磁気旋光分光法のバックグラウンド信号除去能力が正確さを得るのに有効に働いているものと思われる。

試料によっては化学干渉がみられたが標準添加法により上記の相対誤差（±20％）以内には抑制することができた。こうして，直接原子化による迅速分析を容易にすることができた。

一方，種々の元素について，磁気旋光現象（ファラデー効果）の分光学的基礎特性を調べた。その結果，調べたほとんどの元素について4～6 kG の磁場強度（小型の永久磁石で容易に作ることができる強度）で極大感度が得られることがわかった。Cu，Au，Cs，Bi の分析線については旋光強度と磁場強度の関係からゼーマン分裂線間の交叉を新たに発見した。これらの分析線における線交叉は物理分野でも今まで報告がなかった。これに関連して線交叉がない他の元素をも含めて，摂動法を使って超微細構造のゼーマン分裂の理論計算を行い実験結果と比較した結果，良い一致をみた。この理論計算は，本論文では取り扱っていない As，Te，Ti，等，及び希土類元素の原子磁気旋光分光法の分光学的ひいては分析化学的な基礎特性を予測するのに役立つものと思われる。

第2章総括 (Summary of Chapter 2)

本論の第2章においては，多線法の理論，干渉機構の解明への応用，干渉補正への応用について論じた。

励起項エネルギーの異なる複数の原子スペクトル線とイオンスペクトル線の強度を比較することによりそれぞれの励起温度を求め，また，それらの値を用いてイオン化率を求める方法をボルツマン分布の式から誘導した。また，同様にして，分子スペクトル線と原子スペクトル線の強度から原子化率を求める式も誘導した。

この方法，即ち多線法をまず，発光分光分析用励起源の一つである容量結合性マイクロウェーブプラズマ（CMP）でみられた顕著な元素間効果の機構解明に適用した。Mn は多線法に利用できるような比較的強度の強い原子発光線およびイオン発光線を与え，またアルカリ金属およびアルカリ土類元素のような容易にイオン化し易い元素の共存により著しい増感干渉を受けたのでこれをモデルとして研究を行った結果次のことが分った。

(1) 干渉剤の濃度が上がるにつれてイオン化率が下がる。また，その程度は干渉剤がイオン化し易い，即ちイオン化ポテンシャルが低い程，顕著である。

(2) 原子の励起温度もイオン化率と同じような仕方で下がる。

(3) イオンの励起温度は逆に上昇する。

干渉を受ける方の元素のイオン化ポテンシャルと励起エネルギーの異なるものについて Na を共存元素として干渉の効果を調べた結果，イオン化ポテンシャルが高くてイオン化率が低く，励起エネルギーの高い元素（例えばB）の原子発光線は減感効果を受けやすいことがわかった。中間的な

元素の原子発光線は，干渉剤の濃度が上昇するにつれて，最初は増感，しだいに減感の効果を受けることも判明した。

これらのことから，(1)〜(3)の効果が複雑に働いて増感，減感の干渉を生み出していることが分った。この解釈をICPの観測位置に関する干渉の違いについても適用し，原子発光線については，自由電子密度が大きい場合には原子の励起温度の下降による減感効果が支配的に，小さい場合には，イオン化抑制による増感効果が支配的になることを推定した。イオン発光線の増感効果はイオン励起温度が上昇する効果がイオン化抑制の効果を上まわるためであろうと考えられた。また，(2)，(3)の効果は状況によって微妙であり Mn と干渉剤のモル比を一定にすると逆になることも明らかになった。これらの効果がもともとプラズマ中でのどのような反応に起因しているかについては，文献に与えられているように準安定状態の Ar 原子との反応が関与している[I 124]とも考えられるが，複雑であり，どの反応が支配的であるのかは限定できない。しかし，多線法を用いて(1)〜(3)の効果を，種々の系について独立に追究すれば明確にできるものと思う。

次に多線法を上記の Mn に対するアルカリ土類元素の干渉の補正に適用した。(1)〜(3)のパラメータを用いて原子とイオン数の和を求め，発光線強度の代わりに用いたところ，プラズマの円筒対称性が良い場合には干渉が良く補正された。このことは原子とイオンの総数が，干渉が存在している場合でも一定であることを実験的に示しているものと思われる。また，補正が成立したことは，(1)〜(3)のパラメータ，即ちイオン化率，原子の励起温度，イオンの励起温度が干渉の支配的なパラメータであることを示している。

次に，多線法を化学炎における原子化挙動や干渉に適用した。

空気－水素炎中での CuCl → Cu + Cl 反応について，原子化率を CuCl 分光発光と Cu の2本の原子発光線の強度から求め，その炎の高さにおける分布を調べた。その結果，この系においては炎の温度が支配的なパラメータではなく，還元雰囲気が重要な役割をしているのが明らかになった

同様に，空気－アセチレン炎中での Cr と Feについての原子化挙動と化学干渉を多線法を用いて調べた。分子発光としては CrO と FeO のスペクトルのみが観測されたので，これらの発光強度と Cr および Feの原子発光線強度とから，CrO と FeO の原子化率を求めた。原子化率の，炎の高さ方向の分布を多燃料炎と少燃料炎について調べた結果，炎の温度にあまり関係なく還元雰囲気が原子化率に対して支配的なパラメータであることが判明した。次に，以前から現象としては知られていたのであるが実験的な機構解明の研究がされていなかった Cr と Fe間の化学干渉を，原子率および，原子と酸化物の相対的な数，またそれらの総数の変化から調べた。その結果，酸素原子の移動原子化に対する酸化物の相互触媒作用，複合酸化物（例 $CrO \cdot Fe_2O_3$，$FeO \cdot Cr_2O_3$）の生成などの効果が炎の条件によって複雑に変化することが分かった。また，Cr の溶液状態での原子価（Ⅲ とⅥ）によっても，これらの効果において違いが生じることが分った。

次に，多線法を電気加熱原子化器における原子化挙動に適用した。

電気加熱原子化器においては，原子化時の温度が原子を十分に励起するほど高くない（〜3000

K）ので多線法の最も基本的なパラメータである原子の励起温度を原子発光線からは測定できなかった。そこで，原子吸光による励起温度測定の方法をPbの複数の共鳴線を用いて確立した。また，この方法を使えば，ガラス状炭素片原子化器上に分布するPbの励起温度を，1000Kという低い温度からでも測定できることが分った。同様な方法を他の元素にも応用し，それを基に CuCl → Cu + Cl の原子化率を CuCl 発光から求めた。原子化率の変化から，H_2を少量，Arキャリヤーガスに加えると原子化率がほぼ1.5倍になることが分った。このようにして，電気加熱原子化器においても還元雰囲気が重要なパラメータであることを解析的に示した。

以上，得られた結果についてまとめたが，ここで，原子磁気旋光分光法と多線法について，現時点での問題点と，考えられる解決法を述べてみたい。

原子磁気旋光分光法における問題点と対策 (Problems in AMORS and possible ways to overcome them)

原子磁気旋光分光法における第一の問題点は，検量線範囲が原子吸光分光法と同程度（$\sim 10^2$）ではあるが原子発光，けい光分光法（$\sim 10^5$）ほどは広くないということ，即ちダイナミックレンジが比較的狭いということである。これは，主に，光源光と吸光線のゼーマン成分（$\sigma^{\pm}$）との相互作用がそれぞれの線プロフィルの裾の重なりで起こるためであると思われる。原子化器での原子蒸気の濃度が変化した場合，線プロフィルが歪むことにより裾と裾の重なりが直線的に変化しないため，検量線に歪を生ずる。

この問題を解決できるかもしれない方法としては，光源光としてキセノンランプのような連続光を使い裾－裾の相互作用をなくする方法が考えられる。しかし，キセノンランプは単位波長あたりの光エネルギーが低いことと，たとえkWオーダーの強力なランプを使って光エネルギーを上げても次に述べるリーク光の問題もあって高感度を得るのに工夫を必要とすると思われる。もう一つの方法は，裾－裾の相互作用を解消するために吸光線のゼーマン分裂に合わせて光源光の方もシフトさせる方法である。シフト光源としては色素レーザーのようなチューナブルレーザーを使うこともできるが，もっと簡単には光源にも磁場を印加してゼーマンシフトさせる方法が良いと思われる。磁場中で安定に点灯する光源としては無電極放電管が良いが，封入元素の気化の過程を含むので輝度がランプ温度により変動するというような安定性上の問題点がある。また，市販されているランプは利用できる元素の点で制約がある。一方，直流点灯した中空陰極ランプでは，ランプ内での電流の流れる方向と磁場の方向を一致させないと，ローレンツ力により放電が維持されないという問題がある。しかし，高周波点灯をすれば，荷電粒子の自由行路が短かくなるため，ローレンツ力により放電が消えることはないということも報告されている[I 121]ので，中空陰極ランプもゼーマンシフト光源として使うことができるものと思われる。

原子磁気旋光分光法におけるもう一つの問題は，直交した偏光子と検光子における有限の消光比（ローションプリズムで$10^{-3} \sim 10^{-5}$）に起因する光源光のリークである。本研究室ではこのリーク光により生ずるバイアス電圧を$I_{\perp} - kI_{\parallel}$の電気的演算により除いているが，バイアス電圧に含まれる光電子パルスに基くノイズは除去できない。そのために，S／N比が低下し検出下限を下げ

ることにおいて限界が生じている。

これを解決する方法として考えられるのは電磁石を交流または脈流で駆動し磁場を変調することにより変調旋光ををとり出す方法である。変調周波数に同調したロックインアンプで正味の旋光信号を取り出し，直流のリーク電圧とその中に含まれる高い周波数のノイズをカットすることによりS／N比の改善をすることができる。この方法で検出下限が下がれば，ダイナミックレンジの方も拡がることになる。

ここで，上に述べてきたことにも関連して，原子ファラデー効果を用いている原子磁気旋光分光法を，もう一つの磁気光学効果である原子フォークト効果を利用した原子分光法[27,44,45]と比較してみる。

序論においても述べたが，二つの方法の違いは磁場を印加する方向にある。ファラデー配置では磁場は光源光の進む方向に印加する。そして，ゼーマン成分の σ^+ と σ^- に周波数差があるときに磁場強度にほぼ比例した角度で旋光する（一次効果）。フォークト配置では磁場は光源光の進む方向と垂直に印加する。そして，ゼーマン成分の π と $\sigma^\pm$ に周波数差があるときに磁場強度の二乗にほぼ比例した位相差で楕円偏光を生ずる（二次効果）。これらのことから，次のようなことが予測できる。

周波数差は $\sigma^+ - \sigma^-$ 間の方が $\pi - \sigma^\pm$ 間の方より一定磁場では大きいことと，一次効果，二次効果の違いにより，低い磁場においてはファラデー配置の方がフォークト配置よりも感度が高い。特に，吸光線がドップラー拡がりやローレンツ拡がりを生じている場合や，核スピンがゼロでない元素で超微細構造に起因する複雑なゼーマン分裂を生ずる場合においては，π と $\sigma^\pm$ の重なりが，低い磁場では大くなる（例Bi，Au）。このようなときには，前記の傾向が顕著になると思われる。

一方，Stephensが指摘しているように[119]，光源光が幅の狭い線スペクトルの場合においてはフォークト配置では π 成分も相互作用に寄与するので，ファラデー配置で問題になるような裾－裾相互作用に起因する欠点が緩和される可能性がある。

上記の二つの問題は，いずれも実験的には系統的に確認されておらず，また，光源光や吸光線のプロフィルの違いで大きく変化するし，Kerseyらが指摘しているように[I 75]いずれの配置においても複屈折による効果以外に二色性の効果も複雑に寄与しているので，これからさらに種々の実験条件で比較する必要があると思われる。

今一つ挙げておかなくてはならないのは，ゼーマン原子吸光分光法でもそうであるが，光学的にバックグラウンド信号の補正または除去を行っている原子磁気旋光分光法では，試料の直接原子化時に，光源光が通らなくなるほどにバックグラウンド吸光が生じた場合には分析は不可能となるということである。例えば，魚肉などの様に油脂分やタンパク質が多量に含まれる試料の直接原子化の際にはこのような状況が多い。

このような場合には，序論でも引用した分離原子化器を用いるとよいと思われる。ところで報告にもあるように[I 116]，分離原子化器でもベンゼン環を含む化合物やNOなどが多量に発生する

場合には，バックグラウンド信号を完全には分離または除去できないようなときがある。しかしバックグラウンド信号の大きさは小さくなっているので光学的除去方法の能力範囲内には入っている。したがって，二つの方法を組み合わせればバックグラウンド信号をさらに精度よく除くことができるものと思われる。

多線法における問題点と対策 (Problems in Multi — line method and possible ways to overcome them)

多線法における問題点として挙げなくてはならないのは主に以下の事である。

一つは，多線法で利用すべき複数の適当なスペクトル線が感度よく検出できるかということである。実際，例えば，アルカリ元素などのイオン線は，イオンが希ガスの電子配置になるため強い発光を与える共鳴線は真空紫外領域にその波長がある。このため計測が若干面倒にはなるが，光路をArでパージするなどして空気による吸光を防げばよい。

第二の問題は上にも関連するが，多線法における演算には指数項を含んだ式を使うので計測量としてのスペクトル線強度にゆらぎがあると大きな誤差を生ずる。また，このことにも関係するが，一組の複数のスペクトル線の強度を，ゆっくりしたシーケンシャルスキャンなどで一つ一つ計測していると，その間において励起源がいくらか変動してスペクトル線強度がドリフトしてしまい，演算結果に大きな誤差を生ずる。これらの問題を解決できると思われる方法としては，高速スキャンができる分光器で個々のスペクトル線強度をなるべく短時間にサンプリングし，それらをコンピュータで積算し精度を上げる事が良いと思われる。現在，この目的のために，回折格子を2秒に一回転させるマイクロコンピュータ搭載の分光システムを開発中である。

原子分光分析の将来展望 (Future trends in analytical atomic spectroscopy)

最後に，簡単に原子分光分析における将来の方向に対する現時点での予感を著者なりに述べたい。原子化器や励起源などに関する細かな面については，序論においてもいくらかはその将来方向を含ませて論じたので，ここでは，一般的な予感を述べたい。これらの一部は他の分析方法に共通なことかもしれない。

第一に，生体などの複雑なマトリックスを含む試料の直接分析に対するニーズは益々増加するだろうし，それに対して，選択性や感度を向上させる努力は続くであろう。そのためにいままで利用されていなかった原理の応用も，もっと広範囲な分野に渡って行われるであろう。一例としては，磁気光学効果を含めて，選択性を向上させるために外部の力を加えそれに対する選択的な応答を検出するというようなモードが今よりもっと行われるであろう。

第二には，本論文の第二テーマである多線法もそうであるが，試料からの情報の種類を増加する方法が開発されて行くであろう。情報の種類を増加させるには序論で述べたように，複数の異なった方法を結合させるのも一つの方向として考えられる。これに関連して，次の事も重要である。無機分析においてもトレース量における状態分析は益々，その必要性が高まるであろう（例えば半導

体工学や生体分析）が，原子分光分析自体は元素分析であり状態分析の能力は持たない。そこで，イオンクロマトグラフィーなどとの結合が今よりさらに重要なものとして進められるであろう。

このように情報の種類が増えた場合において，そのデータ処理のためにマイクロコンピュータの導入がさらに進行するであろう。こうして複数の種類のデータを総合的に処理することにより今までわかりにくかったパラメータなどが明確に取り扱えるようになるであろう。

上記のような漸次的な発展の他にも，分光分析の方法に使うことができるような新しい現象，素材や素子の開発，または非常に強い社会的要求に伴い，特異的な方法が急に発展するかもしれない（序章表１－１～１－３及び図１に関連して述べたことも参照）。このことに関係するほんの一例として次のことが予想される。光源として今よりもっと容易に利用できるチューナブルレーザーが開発されると，分散系が取り除かれるために，それに関る多数の問題が解消される。このことから，原子分光分析のための方法論は非常に異ったものになるであろう。

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LIST OF PAPERS

Title	Journal	Co-author(s)	Instrumentation associates
1. Application of the Faraday effect to the trace determination of cadmium by atomic spec troscopy	Analyst, **103**, 1021 (1978)	T. Shigeyasu T. Takeuchi	S. Takahashi S. Sakai K. Suzuki R. Katoh
2. Application of the atomic Faraday effect to the trace determination of elements (Cd, Ag and Cu)—effect of the hyperfine structure on the Zeeman splitting and line-crossing	Spectrochim. Acta, **34B**, 389 (1979)	T. Shigeyasu T. Takeuchi	S. Takahashi S. Sakai K. Suzuki S. Satoh
3. Analytical and spectral features of atomic magneto-optical rotation spectroscopy (the atomic Faraday effect) of Sb, Bi, Ag and Cu with a hollow cathode lamp operated in a pulse mode	Spectroschim. Acta, **36B**, 21 (1981)	M. Suzuki N. Aoi S. Tsuge	S. Takahashi S. Sakai
4. Correction system for spectroscopic determination of trace amounts of cadmium using the atomic Faraday effect with electrothermal atomization	Analyst, **104**, 822 (1979)	T. Koyama T. Takeuchi	S. Takahashi S. Sakai K. Suzuki
5. Application of the atomic Faraday effect to the trace determination of lead	Spectrochim. Acta, **36B**, 9 (1981)	T. Nanya S. Tsuge	S. Takahashi S. Sakai
6. Application of magneto-optical rotation spectroscopy to the trace analysis of gold, manganese, cobalt and nickel	Nippon Kagaku Kaishi (J. Chem. Soc. Japan), **1981**, 40 (1981)	N. Aoi S. Tsuge	S. Takahashi S. Sakai

Title	Journal	Co-author(s)	Instrumentation associates
7. Spectral features of atomic magneto-optical rotation spectroscopy (the atomic Faraday effect) and Zeeman splittings of various elements	Spectrochim. Acta, **36B**, 1097 (1981)	N. Aoi S. Tsuge	S. Takahashi S. Sakai
8. Spectroscopic studies of microwave-excited plasma	Anal. Chim. Acta, **60**, 309 (1972)	T. Takeuchi	T. Imura T. Watanabe
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13. Spectroscopic determination of the degree of atomization in an electrothermal atomizer	Anal. Chim. Acta, **113**, 21 (1980)	Y. Ide T. Takeuchi	T. Imura T. Watanabe S. Takahashi S. Sakai
14. Spectroscopic study of atomization processes and inter-element effects on the flame emission of chromium and iron in an air-acetylene flame	Anal. Chim. Acta, **115**, 121 (1980)	M. Yanagisawa T. Takeuchi	
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