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Material Analysis using the Emission Spectrometry

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Guest Article

一般寄稿

Material Analysis using the Emission Spectrometry

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The first direct reading spectrometers were created by Dr HASLER for ALCAN ALUMINIUM. This happened approximatively in 1947. These « direct reading » spark spectrometers have replaced, in most of the applications, the emission photographic plates spectrometers. During nearly 3 decades, the world market has been dominated by 4 manufacturers : ARL (USA), BAIRD (USA) JARREL ASH (USA) and HILGER (U.K.). During this period, the emission spectrometry technique has mostly been dedicated to the spark (metal analysis) and marginally to D.C. arc (powders analysis).

In 1974, some manufacturers have adapted the ICP excitation technique to their simultaneous spectrometer. This powerful technique allows the analysis of liquids.

In 1977, JOBIN YVON created the first sequential computerized ICP instrument and in 1980, the first combined ICP : simultaneous and sequential spectrometer which gave an answer to the question : choice between the cadences of analysis and flexibility in the choice of elements to analyze.

The Emission Spectrometry Department of JOBIN YVON has been created in 1976 as part of JOBIN YVON (created in 1819 !). The Emission Spectrometry Department has known a very high growth (+ 24 % per year) during the 80's. During this period it has developed a complete range of Emission spectrometers dedicated to the elemental analysis of liquids, powders and solids.

At the present time, this range includes :

Spark spectrometers : • JY132 F	for the fast analysis of metals.
GDL spectrometers : • 5000 RF type • 10 000 RF type	dedicated to the thin films analysis in the semi-conductors field, analysis of wafers. dedicated to the thin films analysis for conductors and non-conductors samples. Main application : cars and steel industry.
ICP spectrometers : • JY 124 and JY 238 • PANORAMA and VHR PANORAMA	sequential instruments for analysis of liquid samples. combined instruments : simultaneous with sequential function for analysis of liquid samples.

We will cover the products of the Emission Spectrometry Department in 2 parts :

- analysis of liquid samples by ICP
- analysis of solid samples by spark and glow discharge.

発光分光分析法による物質の分析

Dr. Hasler が1947年に直読式分光器を使った発光分析装置を開発して以来、発光源は金属分析用としては主にスパーク発光が、粉体用としてはDCアークが使われていた。1974年にはICP発光源とマルチタイプの分光器とを組合わせた装置が開発され、液体分析の強力なツールとなった。

当社は、1819年のJOBIN YVON創業以来の分光技術をベースとし、1977年にシーケンシャルタイプのICPを初めて開発した。以後急速に成長し、現在、液体、粉体、固体の元素分析専用の発光分光分析器製品群をラインアップしている（表1）。

ISAでは、分析試料の形態に応じ、次の二種の発光スペクトル分析装置をカバーしている。

- ICPによる液体試料の分析
- スパークおよびグロー放電による固体試料の分析

Analysis of Liquid Samples by ICP

1. Introduction

Inductively coupled plasma (ICP) sources combined with atomic emission spectrometers (AES) are based on the principle that by viewing the appropriate region in an Ar plasma tail flame, the atomic and ionic emission lines of analytes can be measured against very low background emission intensities. The very high temperatures (up to 10,000 K) in the ICP ensure more efficient atomisation than for lower temperature flames such as those used in atomic absorption spectrometry (AAS), and chemical interferences are consequently very small.

ICP-AES exhibit very wide linear response ranges of more than 5 orders of magnitude, making it possible to determine major, minor, trace and ultratrace elements in a single sample preparation. Potentially, up to 70 elements may be measured simultaneously in < 2 min. using < 2 ml of solution. Clearly, such powerful analytical technique has almost limitless applications. as i.e.:

Chemistry - Biochemistry, medicine, forestry and Agriculture - Geology, mining - Environmental protection - Metallurgy and metal production - Cement, glass and ceramics production - Machine and oil condition monitoring - Nuclear reactor engineering and power station - etc...

In this review, we summarise the characteristics of plasma spectrometry.

2. The ICP source

A plasma may be defined as any luminous volume of partially ionised gas. In ICP spectrometry the plasma is generated from radiofrequency (RF) magnetic fields induced by a copper coil which is

wound around the top of a glass torch, as shown schematically in Fig. 1. A sample is generally introduced as a solution, which is first nebulised to form a fine aerosol. The aerosol is transported into the centre of the ICP where it rapidly undergoes desolvation (removal of the solvent from the liquid sample), vaporisation to molecular level and dissociation into atoms, some of which are ionised. Both atoms and ions become excited in the plasma and as they revert to their ground states in the tail flame they emit light (photons). In ICP-AES, their characteristic emission in the tail flame is measured using an optical spectrometer. In ICP-MS, ions are extracted from the plasma into a mass spectrometer for analysis.

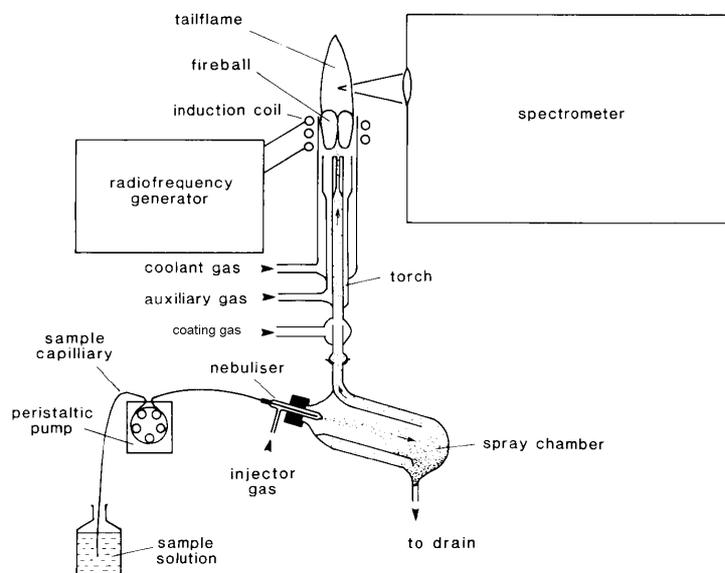


Fig. 1 Sample introduction system used in JY ICP-AES instruments

ICP による液体試料の分析

はじめに

高周波誘導結合プラズマ(ICP)と原子分光分析装置(AES)とを組み合わせたICP-AES液体試料分析法は、高温のアルゴンプラズマを用いるため、原子・イオン発光を非常に弱いバックグラウンド下で測定できる。従って、干渉が少なく、線形応答範囲が広い点が特徴で、2ml以下の試料中から最高70種類の元素を2分以内に同時に測定できる。

ICP 発生源

プラズマの発生の概要を図1に示す。液体試料を霧化して細かいエアロゾル状にしてICP内に送り、高周波誘導加熱されてプラズマ化されたアルゴンで急速に溶剤を蒸発、原子状態に解離して一部をイオン化する。これらの原子とイオンはプラズマ中で励起され、基底状態に遷移するとき発光する。ICP-AESでは、この発光波長と強度を分光器で測定し定性・定量分析する。一方、ICP-MSでは、発生したイオンを質量分析計で測定する。

・ト・チ

当社のト・チは2本の石英ガラス管と1本のセラミック管で構成されており、径が大きいいため、注入速度が遅く、試料の滞留時間が長くなり、発光の確率が高まり信号が大きくなる。

2.1. Torches

The JY ICP torch consists of two concentric glass tubes fabricated from quartz, and a third one fabricated from alumina. The large injector tube diameter (3 mm) decreases the injection speed and increases the residence time of the sample in the plasma, thereby increasing the probability of emission, and, consequently signal amplitude.

2.2. Plasma formation

A water-cooled copper tube is coiled around the upper part of the plasma torch. The coil is connected to a 40.68 MHz solid state RF generator, which creates an oscillating RF magnetic field within the Ar flowing through the torch. Any small variations in plasma impedance are compensated by auto adjustment

Electron density and excitation temperature decrease with increasing frequency, but the argon continuum decreases with the square of the frequency. The overall result using a 40.68 MHz generator is an improvement in the signal-to-background ratio and, hence better limits of detection (LOD) by approximately a factor of four over 27 MHz.

Typical Detection Limits in $\mu\text{g/l}$ at 3 : As 1.2 / Ca 0.03 / Cd 0.09 / Cr 0.15 / Cu 0.18 / Fe 0.19 / Hg 1.2 / K 0.8 / Na 0.3 / P 1.5 / Pb 1.5 / Sb 1.5 / Sc 0.9 / Se 1.5 / Sn 1.3 / Tl 1.0
High frequency RF couples more effectively with the gas flow allowing lower argon flow rates to be used. The lower flow reduces turbulence in the plasma which decreases noise from the background continuum and improves precision. Plasma gas flow rates, generator power, start-up and shut-down are computer controlled and programmable. Safety interlocks are included for coolant water flow, generator power, argon pressure, exhaust flow and drain trap level.

2.3. Plasma gases

Ar is the preferred plasma gas because: (a) it is inert and therefore does not readily react chemically with samples; (b) it has a high first ionisation energy of 15.75 eV, causing effective ionisation of, and emission by, almost all other elements; (c) it is optically transparent; and (d) it has a

moderately low thermal conductivity, so that heat is retained in the plasma fireball enabling stable operation at moderate power inputs.

Inside the plasma, the "normal analytical zone" (NAZ) is characterised by an incredibly low intensity of background emission and is consequently nearly invisible until a sample is injected. Here, the emission spectrum exhibits a continuum with a relatively small number of discrete lines produced predominantly by Ar atoms. The large transfer optics of the JY spectrometers allow viewing of the entire 6 mm high NAZ at once. By viewing all of the emission zone at one time, optimization of conditions on one element gives excellent results on all elements.

Samples are injected into the centre of the plasma, and so pass through the centre of what is effectively a very high-temperature tube-furnace. There is little inter-mixing of the sample with gases in the plasma fireball. The sample is heated rapidly to ~ 8000 K by conduction, convection and radiation effects, and sample molecules undergo nearly instantaneous desolvation, vaporisation, dissociation, ionisation and excitation. The high temperature of an ICP ensures that dissociation is highly efficient and, unlike flame atomic absorption spectrometry (FAAS) and DCP-AES, chemical interferences (caused by the recombination of atoms and the formation or retention of stable molecular species in the flame) are negligible. Similarly, ionisation interferences are also generally insignificant.

3. Sample introduction

The purpose of the sample introduction system is to produce an aerosol from a sample and introduce it into the ICP where excitation occurs. The basic components consist of a nebulizer, spray chamber and torch all of which play a major role in the quality of the analytical results.

Sample introduction for plasma spectrometry is generally accomplished using solution nebulization. Sample solutions are aspirated by a nebulizer (Fig. 1) which shatters the liquid

・プラズマ形成

プラズマ・トーチ上部に巻いた水冷銅製コイルに高周波(40.68MHz)を印加し,アルゴンガス流に振動高周波磁場を形成する。周波数を高くすると,電子密度は減少するがバックグラウンドが下がる。さらに,ガス流との結合効率が向上し,アルゴン流量を減らせるので,バックグラウンドノイズが減少して精度が向上する。各元素の検出限界は表1を示す。

・プラズマ・ガス

アルゴンは,不活性,高い一次イオン化エネルギー(15.75eV),透明性,低伝熱性のため,プラズマ・ガスに適している。プラズマの標準分析領域(NAZ)からの背景放射は非常に小さく,試料投入して始めて,連続放射中の少数の輝線スペクトルが確認できる。ISA製品の光学系は大型で6mmのNAZ全体を一度に測ることができるため,一つの元素について最適化すれば,元素ごとに観測位置を再調整する必要はない。試料はプラズマ中で8000Kまで急速に加熱され,脱溶剤,蒸発,分解,イオン化,励起がほぼ瞬間的に行われる。ICPは高温なため分解効率が高く,フレームレス原子吸光分析や直流プラズマ原子吸光分析とは違い,化学的干渉やイオン化干渉は殆ど無視できる。

into fine droplets using an Ar gas stream of ~ 1 l/min. These droplets are directed into a spray chamber which removes the unsuitable larger (~ > 10 μm) material, and allows only the finest spray to pass into the plasma. The low injector Ar gas flows required in ICP spectrometry result in the efficiency of this nebulisation and sorting process being very low, typically only ~ 2% of the sample solution aspirated being transferred into the plasma.

No single introduction system is optimal for all types of samples. JOBIN-YVON has designed several systems in the form of individual cassettes permitting rapid interchange. Within a few minutes all hardware can be replaced without realignment. The following cassettes are available for the following applications: (1) Standard aqueous with cyclonic spray chamber and pneumatic nebulizer, (2) High salt content solutions and high solid suspensions, (3) HF containing solutions, (4) Ultrasonic nebulization, (5) Hydride generation and (6) Solid sample introduction by spark ablation.

<Patented Sheath Gas>

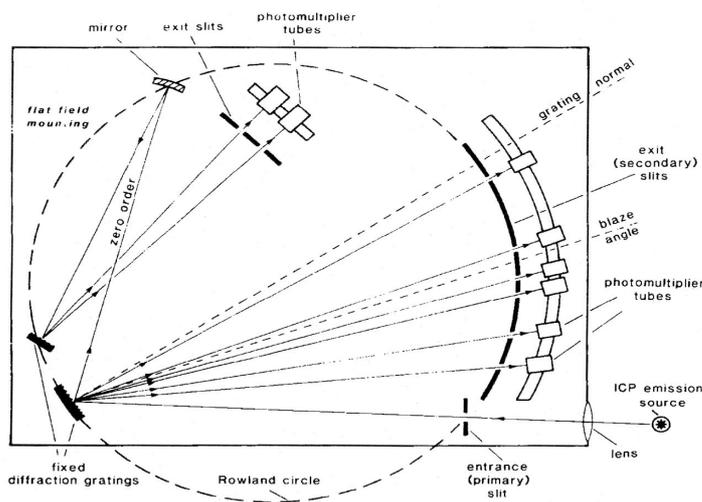
Mounted between the spray chamber and the injector, the sheath gas device enhances performance and stability by injecting a computer controlled, axial flow of argon around the aerosol prior to its insertion into the injector.

For samples with high salt content, e.g. 30 % NaCl, this minimizes contact of the sample with the injector wall and eliminates crystallization at the injector tip. The injector's uniquely large bore, 3 mm, also contributes to the ability to handle high solids such as slurries, and serves to improve detection limits by increasing the residence time of atoms in the plasma. An optional argon humidifier provides a moist nebulization gas which minimizes clogging of the nebulizer with high solids.

When alkali elements are to be determined, the sheath gas flow is automatically adjusted to optimize the con-

ditions for these easily ionized elements allowing a 7-10 fold improvement in their LODs.

- (a) A Paschen-Runge polychromator : The additional flat field mounting enables the determination of the alkali metals (K, Li, Na) which have their most sensitive Lines in the 500 -800-nm range.



- (b) A Czerny-Turner monochromator. contains only one (or two inter-changeable) photomultiplier tube(s) combined with a movable diffraction grating.

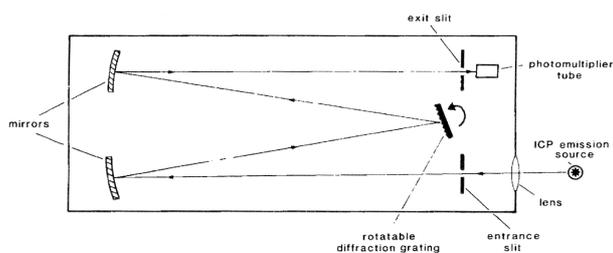


Fig. 2 Schematic representations of two major types of ICP-AES spectrometers.

試料の導入

試料溶液は1l/m未満のアルゴンガスでネブライザーを用いてエアロゾル化し、スプレーチャンバで直径10 μm以上の液滴を除いた上で、プラズマ中に噴射する。プラズマへの試料溶液の導入量は2%未満である。当社では、様々な試料に対応するため、標準、高塩濃度用、HF用、超音波ネブライザ、水素化物発生器、固体試料用スパークアブレーションなど各種のカセット式サンプリング装置を用意している。

・シ・ス・ガス装置

シ・ス・ガスでエアロゾルの周囲をアルゴンガスで軸方向に包むことにより安定化・高感度化をはかっている。アルカリ元素ではシースガス流量を最適化することにより検出限界(LOD)が7~10倍改善される。インジェクタの孔径が大きい(3mm)こと、加湿装置などにより先端のツマリは少ない。本機構は当社の特許となっている。高周波誘導結合プラズマ - 原子発光分析法(ICP-AES)

多種多様な元素を定量するには、複雑な発光スペクトルを元素ごとの波長に分離し、光の強度を正確に測定する必要がある。

4. Inductively coupled plasma-atomic emission spectrometry (ICP-AES)

Quantification of elemental abundances in samples by ICP-AES is based on the ability to separate a complex emission spectrum into its component wavelengths, with sufficient sensitivity and resolution to precisely measure light intensities at the characteristic wavelength of each analyte. Schematics of typical ICP-AES systems are shown in Fig. 1 and Fig.2.

4.1 Spectrometer design

There are two major categories of ICP-AES spectrometer (Fig.2): polychromator (simultaneous), and monochromator (sequential) systems. Both are capable of measuring the full range of wavelengths used in AES, typically from the upper part of the vacuum ultraviolet (160 nm) to the limit of visible light (780 nm). Special MgF₂ optics and detector permits also the analysis at 134 nm.

Simultaneous spectrometers are direct reading designs (Fig. 2a). Light is focussed onto a fixed diffraction grating which splits the light into its component wavelengths. Exit slits located at pre-determined positions around a Roland circle are used to focus light of specific wavelengths onto individual photomultiplier tubes for measurement. The number of elements which can be determined simultaneously is limited by the physical space required to position photomultiplier tubes for adjacent wavelengths, up to 47 elements to be measured simultaneously. For the determination of elements such as P and S which have their optimum analytical wavelengths in the vacuum ultraviolet (< 200 nm), the spectrometer and its associated optics are purged with N₂. One major disadvantage of polychromators is their high cost, because they require a separate suite of electronics for every analytical wavelength installed. They are also relatively inflexible, since analytical wavelengths are best chosen before the instrument is assembled. These limitations are not as great as might be expected, because in reality there is often only limited choice of analytical wavelengths. A POLYSCAN function permits to scan the spectrum over 4.4 nm in front of each particular

photomultiplier. Each detector becomes then a monochromator and brings the flexibility to the polychromator. The main advantages of polychromator systems is their speed of analysis and low running costs, since they potentially enable the determination of 47 elements in 1-2 min., using only 1 - 2 ml of sample solution. In practise the number of elements which can be quantified is limited by the sample type and the sample preparation procedure employed, and a maximum of 25-30 elements is a more realistic expectation for simultaneous analysis. Finally, the simplicity of polychromators ensures reliable operation and optimum short and long-term reproducibility. Sequential systems are based on computer controlled scanning monochromators (Fig. 2b), which can be pre-programmed to drive rapidly from line-to-line, measuring sequentially at each analytical wavelength chosen. Such systems are inherently cheaper and more flexible than polychromators because they can measure any wavelength required. The main disadvantage of the monochromator is speed, since the analysis time is directly proportional to the number of elements being determined. A 20-30-element programme which requires 1-2 min. per sample on a polychromator will typically take 5-10 min. on a monochromator, depending on the integration times and number of the elements. The volume of sample solution consumed will also be increased accordingly. Combined spectrometers employing both a polychromator and a monochromator provide optimum performance and flexibility but are correspondingly expensive.

<Setting a new standard...>

Figures of merit for ICP systems were described in an article in Applied Spectroscopy, Vol. 49, No10, 1995 (12A-18A). When the JY 238 ULTRACE is compared to these figures, it has a perfect score. It is the only ICP today that can make this claim.

・分光系の設計

ICP-AESには、ポリクロメータを用いる(同時多元素分析型)とモノクロメータを用いる(シーケンシャル式)の二方式があり(図2)、両タイプとも160nm～780nmの波長域が測定できる。(MgF₂窓と特別な検出器を使うと134nmが可能)

同時型(図2a)は、ポリクロメータで分光後、ローランド円上の出口スリットを通過、光電子増倍管で検出する。最高47種までの元素が同時に測定できる。このタイプは、分析対象波長ごとに電気系が必要で、コストが高く、融通性に欠ける。長所は、わずか1～2mlの試料で同時に多元素の定量ができるため、分析速度が速くランニングコストが低いことである。なお、当社のPOLYSCANを使うと測定波長が広がり融通性に富む。一方、順次式(図3b)は分析対象波長を順次取出し測定するため、未知試料の分析は容易だが、分析時間が長くなり、試料の消費量が多くなる。

ICP方式の中で最も高性能なJY 238 ULTRACEの仕様を表1に示す。

・放出スペクトル、干渉、輝線の選択

ICP-AESは、他の分光法と比べ干渉を受けにくい、輝線が重複する場合には問題となる。また、プラズマや分光器の迷光、輝線の広がり、とくにAl, Mg, Caによるバックグラウンド放射の増加が問題となる。

Table 1 Figure of merit for ICP system

Figures of Merit	Measurements	Best Results	JY ULTRACE
Number of elements	Wavelength range	120-770 nm	120-800 nm
Selectivity	Ba(II) 230 nm line profile	5 pm	< 5 pm
Repeatability	RSD Mg(I) 285 nm line	0.2 % RSD	< 0.2 % RSD
Long-term stability	Warm-up time	15 min	< 10 min
	Long term	% RSD \leq 1 %	< 1 % RSD
Robustness	Mg(II)/Mg(I) ratio	\geq 10	> 10
Limits of detection	SBR Ni 1 ppm	\geq 30	> 30
	RSD background	< 0.3 % RSD	< 0.3 %
Accuracy	Calibration procedure	-Change in number of standards -Rejection of outliers -Possibility of weighting -No blank -Standard addition method	Yes Yes Yes Yes Yes

4.2. Emission spectra, interferences and line selection

ICP-AES is less susceptible to interferences than most other spectrometric techniques, but the coincidence or overlap of emission lines remains a serious analytical problem. Many elements have large numbers of individual lines, Fe alone, for example, exhibiting > 1000 separate atomic and ionic lines between 200 and 300 nm. Compilations of ICP-AES lines and spectra provide vital information on potential spectral overlaps.

ICP emission spectra are also characterised by background continua. The background spectrum is not only due to emission from the plasma itself but also originates from stray light within the spectrometer, recombination radiation and line broadening effects. Background enhancements caused by Al, Mg and Ca are particularly problematic.

Line selection and the identification and correction for spectral interferences is one of the most critical aspects of successful ICP-AES analysis. The use of holographic grating, long focal length and simple optical mounting reduces the level of background, of stray light and enhance the resolution. The actual lines chosen by the analyst will depend on a number of factors including the resolution,

sensitivity and other characteristics of the ICP-AES instrument employed, and the composition of the samples being analysed.

うまいICP-AES分析には、輝線の選択、スペクトル干渉の特定と補正などが重要である。ホログラフィック回折格子と長焦点で単純な光学系を使うと、迷光によるバックグラウンドを減らし、分解能を向上させることができる。

Analysis of materials by Spark Emission

1. Introduction

Spark emission spectrometry is a rapid, precise and reliable method for elementary analysis of conductive solids.

Spark instruments are used on a systematic basis in the steel, metallurgy and foundry industries for developing, producing and providing quality control of metals and alloys.

Most elements are analysed directly and simultaneously including C, S and N at traces (from a few ppms) to major levels (several percents).

2. Source

A "spark" analysis consists in a succession of individual sparkings (each one with a duration of about 100 μ s) during a short period of time (usually less than 10s). Each sparking melts a small area of the sample to be analysed leading to the emission of a composite light.

For each element, a characteristic spectrum is emitted - formed by lines at specific wavelengths which correspond to the transitions between the various levels of energy of the cloud of electrons of this element. The intensity of the emitted lines allows, under well defined excitation conditions, the elements content to be measured.

3. Spectrometer

The optical system of a spark instrument consists of a polychromator which scatters the spectrum and isolates the analytical lines of the elements to be analyzed. In the JY 132F, a 50cm focal length Paschen Runge-type polychromator is used. It consists of an entrance slit, a con-

cave grating and exit slits. The slits, the center and the apex of the grating are located on a circle, known as Rowland's circle.

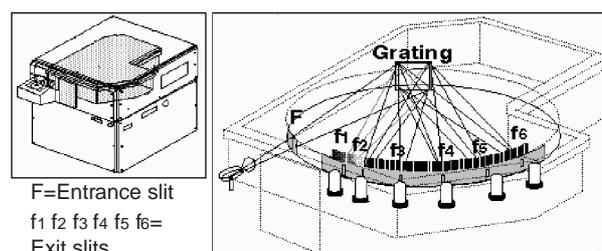


Fig.1 Principle of the polychromator

As a polychromator's performance basically depends on essential features such as brightness, stability, spectral purity and resolution, let's see how the various components of the system contribute to its performance, starting with the grating.

The diffraction gratings were initially engraved, then holographic. The last generation is that of the so called "blazed" holographic grating, whose mirroring angle is obtained by ionic machining.

Engraved gratings are cut line by line on special machines. Despite the very high precision of the engraving machines, these gratings may incorporate engraving errors which cause phantom spectra (ghosts) and stray light.

For holographic gratings, a polished support covered with photosensitive resin is exposed to the interference of two laser beams and processed chemically. This process allows strictly parallel and equally-spaced lines to be obtained.

スパーク発光による物質分析

はじめに

スパーク発光分光分析装置は、鉄鋳、冶金、鋳物分野において主に品質管理用として、固体中の元素分析(ppm ~ %)に幅広く使われている。

スパーク発生源

通常約10秒間、100 μ s間隔で試料をスパーク発光させ、そのとき形成されるプラズマから発せられる光の強度により定量分析を行う。

分光器

当社のスパーク発光分光分析装置JY132Fでは、焦点距離50cmのパスシェン・ルンゲ式ポリクロメータ(図1)を使っている。

ポリクロメータの性能は構成する光学部品、中でも回折格子の良否に左右されるが、当社の装置にはブレード・ホログラフ回折格子を採用している。従来のルーリングエンジンによる回折格子では周期的な誤差が問題になる。一方、ホログラフ型では、溝が正弦波状になるため、迷光は少ないが明るさに問題があった。ブレード・ホログラフ回折格子では、イオンエッチング法を導入し、ブレード角を持つことにより、明るさが格段

The grating is free of phantom spectra and stray light. However, the brightness achieved by the conventional holographic gratings is not as high as that of engraved gratings, as line profile is sinusoidal.

To achieve gains in terms of brightness, this profile is machined by ion bombardment, to achieve an echelle type profile according to the selected mirroring angle (blaze angle). Such blazed holographic gratings are much brighter than conventional holographic gratings.

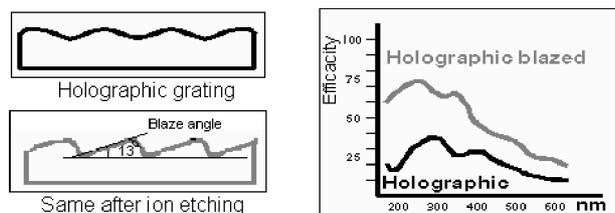


Fig.2 Light efficiency holographic grating with ionic etching

For a given grating and in a given order, the resolving power is proportional to the focal length of the optical system and to the reciprocal of the entrance and exit slit width. Let us remind that it is exactly the opposite for the brightness.

To achieve the resolution necessary for analyses (considering that the spark lines are larger than the ICP lines), one can increase either the focal length of the system for a given grating, or the number of lines of the grating for a given focal length.

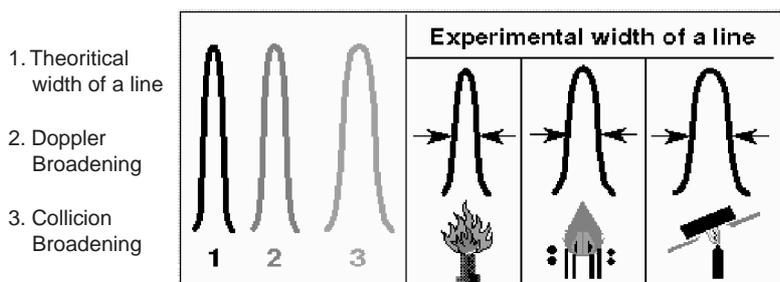


Fig.3 Line broadening in Spark compared to ICP

に向上した(図2)

スパーク発光分析装置では、発光スペクトルの幅がICPより広がるため(図3)、焦点距離を短くしたり、溝の数を減らすことができる。分光器が明るい装置の安定化がはかれ、検出感度が良くなる。焦点距離0.5mの小型装置は安定性が抜群で、3600本/mmの高輝度ホログラフ回折格子を備えていれば、分析には十分な分解能が得られる。

分析対象元素の選択は、ポリクロメータの出口スリットとして金属マスクを置いて行うが、JY132Fは約200本のスリットやマスクを備えており、殆どの元素分析に対応可能である。必要に応じ測定波長幅を広げることにより光学アライメントやバックグラウンドの影響の解析できる機能はPolyscan System(図4)として当社の特許となっている。

分析装置

JY132Fは、Windowsタイプの生産管理用装置で、ISO認証に必要な分析の質とトレーサビリティを保証できる。JY Metaltestという異物判別用ポータブルタイプも取り揃えている。

When the system's focal length is increased, its mechanical stability is impaired and, for the same grating, brightness is reduced. Stability is a critical characteristic for equipment which must retain its calibration characteristics over a long period of time. Further, brightness is invaluable as it is synonymous with good detection limits.

Thus, a compact optical system with a 1/2 meter focal length offers excellent stability. Resolution is adequate for analyses if the system is equipped with a grating with a high resolution (3600 lines/mm) and high brightness (blazed holographic).

In an emission spectrometer, the exit slits of the polychromator isolate the lines corresponding to the elements to be analyzed. This is the spectrometer optical layout.

Among the many lines of an element, a selection of a few lines is adequate to meet most analytical requirements. This is the reason why the JY132F polychromator is equipped with a metallic mask of about 200 lines, allowing all possible elements in the usual matrices to be dosed at various concentrations.

When the mask is aligned, all its slits are aligned.

Only the slits of the optical programme of the instrument are kept opened but further on site extensions are easy.

It may be advantageous to explore the spectrum on either side of each line, either over a short distance, to check spectral alignment, or over a medium distance, to assess the influence of the emission background, or over a larger distance to use other analytical lines.

This is done by the Polyscan (JY patent) system which consists in the movement of the entrance slit along the Rowland system.

4. Instruments :

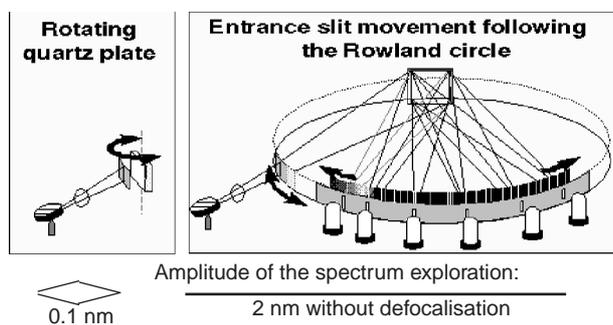


Fig.4 Principle of the Polyscan

The JY132F is a laboratory instrument for production control. Equipped with the JY Windows software it guarantees the quality and the traceability of the analysis, essential part of the ISO certification.

The JY Metaltest is a mobile instrument and can be brought on site to sort the scraps or, to identify final products and prevent mix ups before despatching.

Glow Discharge Optical Emission Spectrometry

1. Introduction

For many industrial applications, it is essential to know the chemical composition of the product, both at the surface and in the bulk. Whether the application is coated steels, e.g. for car bodies, or semiconductor wafers, e.g. for integrated circuit manufacture, the surface composition determines many important parameters such as appearance, corrosion resistance, adhesion, conductivity, etc, while the bulk composition is important for the stability and long life of the product.

Only one technique, Glow Discharge Optical Emission Spectrometry (GD-OES) can provide both the surface and bulk composition, quickly, cheaply, and with high sensitivity to all elements (including the gaseous elements), for almost all solid materials, including metals, metal alloy coatings, semiconductors, polymer coatings, powders, glass, ceramics, etc.

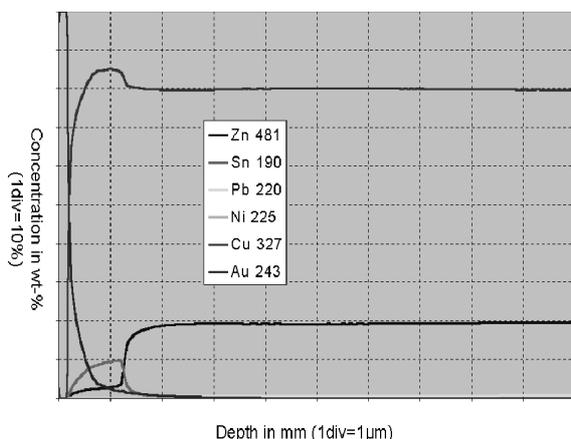


Fig.1 Depth profile analysis of a gold coated watch bracelet

As the name suggests, GD-OES combines a glow discharge source (GD) with an optical emission (OE) spectrometer. Glow discharges will be familiar to many readers from experiments at school or university. A glass tube containing two metal electrodes is filled with a low pressure of argon, then a potential is applied across the two electrodes. A plasma is created inside the tube and the tube is seen to glow.

2. Source

The source now used in GD-OES is quite different in detail from the glass tubes used in teaching laboratories. The cathode is replaced by the sample to be analysed while the positive electrode (anode) is a hollow metal tube.

When a potential is applied, argon ions are generated which will be attracted to the sample where they impact with sufficient energy to knock atoms off the surface.

These «sputtered» atoms then enter the plasma where they are excited by collisions. Then they de-excite by optical emission, hence the «glow». De-exciting atoms emit photons with characteristic wavelengths (e.g. Fe at 371.994 nm or H at 121.567 nm). By measuring the signals at these wavelengths, we can then measure the numbers of each type of atom coming from the sample.

The inside diameter of the tube, or hole, is typically 4 mm. The tube is positioned very close to the sample surface, typically 0.1-0.2 mm. This ensures that sputtering of the sample occurs only in the area of the sample opposite the hollow tube.

グロ-放電発光分析装置

はじめに

様々な産業分野で、材料の全体(bulk)および表面の組成を正確に把握することは必要不可欠である。現在、金属、半導体、コーティング膜のほか各種材料の元素組成(バルクと表面)を、素早くかつ安価に検出できる分析法は、グロ-放電発光分析装置(GD-OES)ただ一つである。図1に金メッキをした腕時計のバンドの深さ方向の組成分析結果を示す。

GD-OESは、字義通りグロ-放電源(GD)と分光分析装置(OES)を組み合わせたもので、低圧アルゴン中でのグロ-放電による発光スペクトルを測定する。

グロ-放電源

現在GD-OESでは、陰極に分析試料が、陽極には中空の金属管が使われている。電圧を印加するとアルゴンイオンが生じ、陰極から試料の原子がたたき出され、プラズマ中で励起される。この励起原子が基底状態へ遷移するときに放出される光の波長と強度から、試料の元素を定性・定量分析する。

陰極管の内径は約4mmで、試料表面に非常に近接させているため、高周波パワーとガス流量を上手く調節すると、特定部分の試料を急激にスパッタリングすることができる(図2)。

When the operating conditions of the source are chosen carefully, for example, at specific values of argon pressure and applied rf power then uniform and rapid sputtering of the sample occurs.

(Nota : The potential applied to the sample is varying at high frequency for both conductive and non-conductive samples to be analysed with one source).

Sputtering rates are typically 1-10 μ m/min, equivalent to about one atomic layer every 6 ms. Since optical signals can be recorded at ms speeds for many minutes, it is possible, in GD-OES, from the one sample, to record signals from the first atomic layers of the surface down to depths of tens of micrometres.

Thus, in this rather complex process, the sample is sputtered

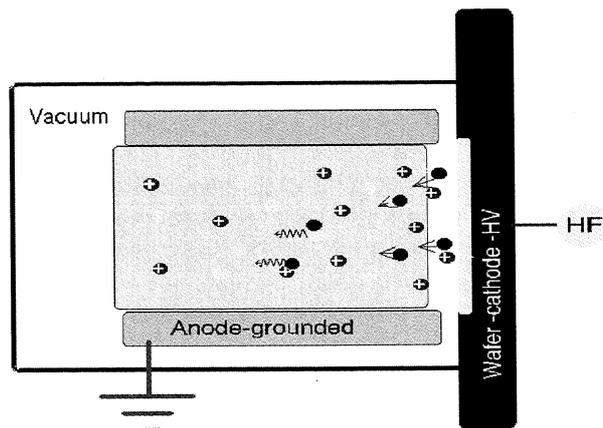


Fig.2 Principle of a glow discharge

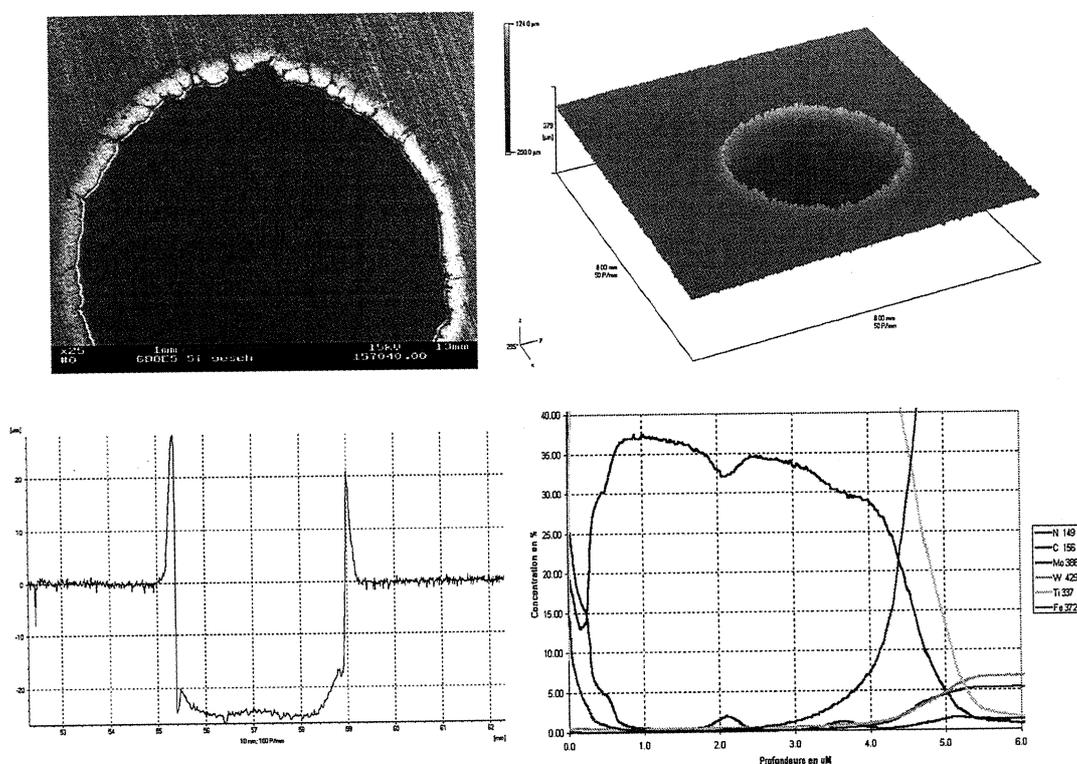


Fig.3 Record of a crater shape and depth profile analysis

通常スパッタ速度が1～10 μ m/min, ミリ秒単位の発光を記録するため, 表面原子層から数十10 μ mにわたる組成の深さ分析ができる。高周波を用いた当社のGD-OESは, 導電性, 非導電性いずれの試料も測定できる。図3にクレータの形状と深さ分析例を示す。

分光器

GDで生じた光はポリクロメータまたはモノクロメータでスペクトル解析されるが, ポリクロメータでは各元素毎に検出器を備えた構造となっている。図4に自動車用鋼板の深さ方向の定性・定量分析結果を示す。

分析装置

当社では2種類のGD-OPSを製品化している。

- ・JY5000Rf: 本機は50cmのポリクロメータが特徴で, ウエハの品質管理用として自動機を日本のデバイスメーカーに納入している。図5にBPSGの深さ分析の例を示す。
- ・JY 10 000Rf: 本機は1mのポリクロメータによる高分解能が特徴で, R&D用として優れている(図6)。

and an optical signal is produced which measures the composition of the sputtered material.

3. Spectrometer

The optical signal emitted by the sputtered atoms leaves the source through a window and is focussed onto the entrance slits of one or more spectrometers (polychromator or monochromator).

If the instrument contains only one spectrometer, it is usually a polychromator with a number of fixed channels, one for each characteristic wavelength (element) of interest.

The principles of spectrometers have been described previously for Spark and ICP.

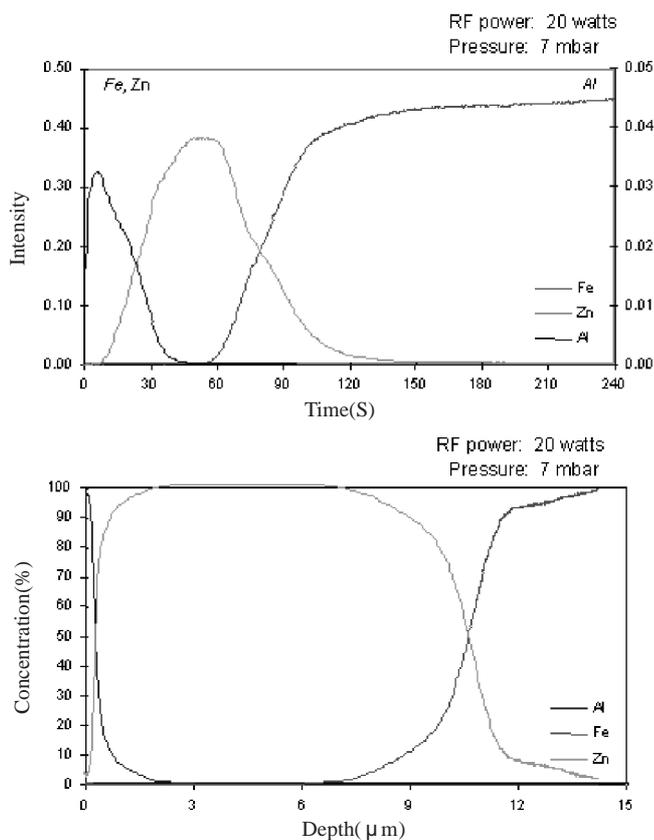


Fig.4 Quantitative depth profiles: Al on Zn on steel, for automotive

4. Instruments

2 instruments are proposed which differ by their optical resolution.

The JY 5000Rf features a 50cm poly and is an ideal instrument for production control. 2 dedicated versions of this instrument coupled with a robot have been delivered to one of the leading semi-conductor manufactures in Japan for the monitoring of wafers.

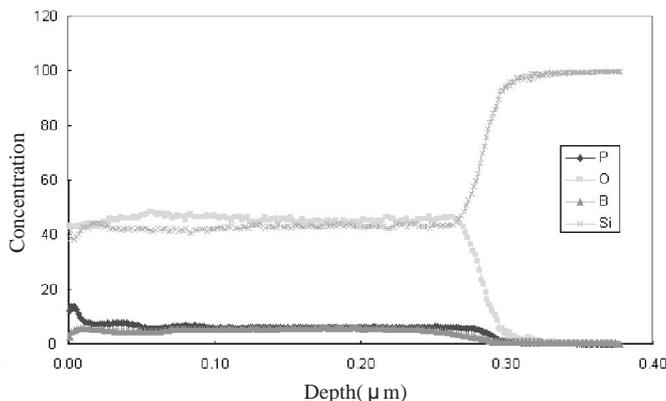


Fig.5 Example of quantified depth profile of a BPSG

The JY 10 000Rf (with a 1m polychromator) offers an unmatched resolution and is the instrument for complex applications and research.

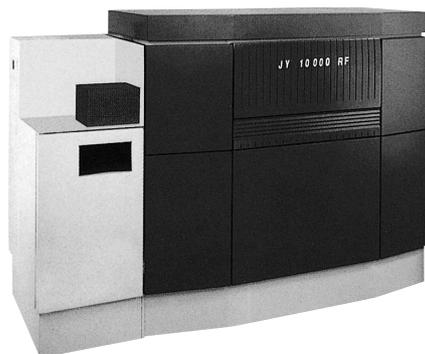


Fig.6 Glow discharge optical emission spectrometer JY 10 000RF



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