

OPTICAL EMISSION SPECTROCHEMICAL ANALYSIS

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Abstract - In optical emission spectrochemical analysis the analytical signal consists of the emission line spectrum of the free gaseous atoms or ions of the original sample. Therefore a representative part of the sample has to be brought into this radiative state with the help of the spectrochemical excitation source. The unique role that the source plays is reflected in the first part of the lecture covering amongst others the DC arc under the influence of external magnetic fields, stabilized arc and spark discharges for improved precision and accuracy, high repetition rate spark sources, electrical discharges under reduced pressure especially the glow-discharge lamp according to Grimm and laser sources for sampling and excitation respectively.

In the second part of the paper the present state and future aspects of other parameters relevant to OES will be surveyed, i.e. spectral apparatus (which is of much more significance in emission than in atomic absorption spectroscopy), the unique properties of the photographic emulsion as radiation detector in combination with automatic recording spectrum photometers and computerized handling of the data. Finally an evaluation is made of the respective virtues of different kinds of photo-electric radiation receivers, e.g. silicon photodiodes and arrays composed of them, image detector tubes and television camera tubes.

INTRODUCTION

Optical Emission Spectrochemical Analysis (OES) was for a long time one of the main methods for industrial applications where high throughput of samples combined with sufficient precision and power of detection was of paramount importance. As other competing methods have become available, e.g. atomic absorption and atomic fluorescence spectrometry, X-ray spectrometry, activation analysis, spark source mass spectrometry, there is justification in evaluating the present importance and future aspects of OES. For this purpose some of its fundamental properties are first recalled:

1. OES offers true multi-element analysis facility, i.e. the simultaneous determination of a large number of elements in a wide variety of sample material, solid as well as liquid, electrically conducting as well as non-conducting. This has led to the development of powerful universal methods.
2. Common to all emission methods and contrary to absorption methods a large range of concentrations can be covered by a single measurement.
3. OES is operated as a relative method. It affords calibration with the help of standard samples of known composition.
4. Small sample consumption. 100 mg can be considered as an unlimited amount of sample, 10 mg are usually sufficient, microsamples ranging from 0.01 to 1 μg can be analysed with the help of special methods, e.g. using lasers or microwave discharges.
5. High specificity. The analytical results are unequivocal.
6. High selectivity. One element can be determined in the presence of many others. This is a result of the high information capacity. Of the large number of spectral lines comparably few are needed.
7. The power of detection is often satisfactory, limits of detection ranging from 10^{-4} to $10^{-8}\%$, depending on element, matrix and radiation source. Fig. 1 gives an example. Because of the high selectivity and good power of detection in many cases chemical pre-concentration may not be necessary.

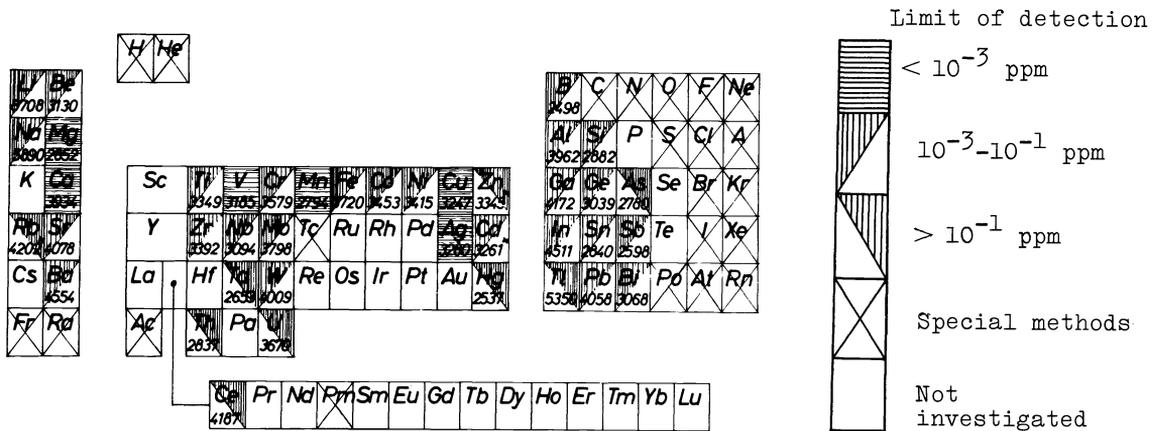


Fig. 1. Spectrochemical analysis of traces in graphite

8. Precision may be of the order of 10% at low concentrations and about 1% at medium and high concentrations, again depending on the analytical problem and on the chosen procedure.
9. Accuracy may be effected by matrix effects, but it can be high, especially with some of the new methods, if calibration is done critically and the scope of applicability carefully tested.
10. Because of the small sample consumption it can easily be combined with chemical pre-treatment or enrichment procedures.
11. It may be used for the testing of other methods especially during the course of their development. It is also very useful as a rough, but fast semi-quantitative method preceding other special methods aimed at high power of detection or high precision.
12. OES is well suited for production control as large numbers of sufficiently precise analyses can be executed in short times, once the whole procedure has been worked out in all details, which may be tedious and time consuming.
13. Automatization and computerization is possible with a corresponding increase of speed and reliability as well as a saving of manpower and costs. It is no question that in future analytical needs will rather increase than decrease, e.g. due to the following reasons:

Increasing scarcity of raw materials, recycling of materials, tighter production control to save precious materials, environmental protection. Although OES is an old established method and dramatic new developments therefore should not be expected, it nevertheless happened that a recent revival of interest has led to rather unexpected progress in all fields of OES with some exciting things still to come.

Recent progress and its relevance to future possibilities will be reported with the help of some well-known key-words. Because of the complexity of the subject a rather personal selection has been made.

The analysis of liquids which is mostly done with the help of electrical flames or plasmas is covered by another paper. The analysis of gases by OES is rather uncommon. Therefore, this paper will mostly deal with the analysis of solids, a field of application where OES often offers unique solutions to complicated analytical problems.

RADIATION SOURCE

The analytical signal, i.e. an emission line, is produced by the excitation of free gaseous atoms or ions. Therefore a representative part of the samples has to be brought into this state. The eminent role of the spectrochemical radiation source in which this is done will be reflected in its rather more extensive treatment.

The electrical DC-arc is still indispensable as the radiation source for the analysis of electrically non-conducting powder samples, common in mineralogy, geochemistry etc. High power of detection combines with true multi-element facility for a large variety of samples. Numerous universal methods, some of

which have been well known for a long time, offer rapid semi-quantitative determination of numerous elements (e.g. 1,2,3). Careful investigation into chemical and physical properties has resulted in improved versions (e.g. 4,5,6,7).

By applying homogeneous as well as inhomogeneous magnetic fields to the DC-arc better power of detection, higher precision and better control of sample evaporation has been achieved (8,9) Fig. 2. Much larger amounts of samples than otherwise possible can be consumed. Therefore application in mineralogy and geochemistry, especially for the analysis of heterogeneous samples, is recommended.

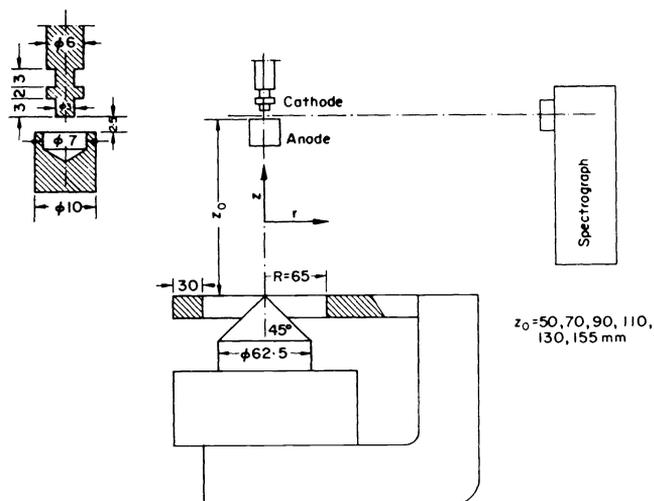


Fig. 2 Schematic view of the magnet and DC-arc - spectrograph system (Courtesy authors) (8)

In another DC-arc version, i.e. the Gordon arc, careful control of excitation conditions has led to the development of a fast universal method for the analysis of small solid and liquid random samples, combining high absolute power of detection with a precision described by about 10% relative standard deviation. One of its many unusual and interesting features is shown in Fig. 3, i.e. the effectiveness of intensity control rather than current control of the arc.

The direct analysis of powders using arc or spark excitation has not become very popular outside the USSR and some other countries in Eastern Europe. An example is shown in Fig. 4. This may be due to some disadvantages of these methods, i.e. incomplete vaporization of the small particulates during the short time of residence in the hot plasma.

Whereas it is difficult to obtain very fine grain powders by grinding which are necessary for reliable direct analysis, it has now become possible to directly produce aerosols, at least from metals, with very small grains (Fig. 5).

The aerosol can then be analysed with the help of almost any radiation source, e.g. with the induction coupled plasma. A hand-held aerosol generator for remote analysis has recently become commercially available which can be used within about 17 m distance from the excitation source and spectral apparatus (Fig. 6). With such a device large objects can be analysed in situ.

Spark discharges are generally used for high precision analyses of metals, mostly in production control. Until recently because of matrix effects the range of samples which could be analysed with the help of one set of analytical curves was rather restricted. By remelting the surface of the sample in high power, unidirectional, medium voltage, pre-spark discharges in Ar-atmosphere (12), sometimes combined with a higher repetition rate (13), matrix effects could be drastically reduced and calibration made much easier. Originally developed for the analysis of steel, this method has also been very successfully applied to the analysis of aluminium and its alloys (14). Metal analyses with a relative standard deviation of 1 to 2% belong to industrial routine, less than 1% are obtainable in favourable cases.

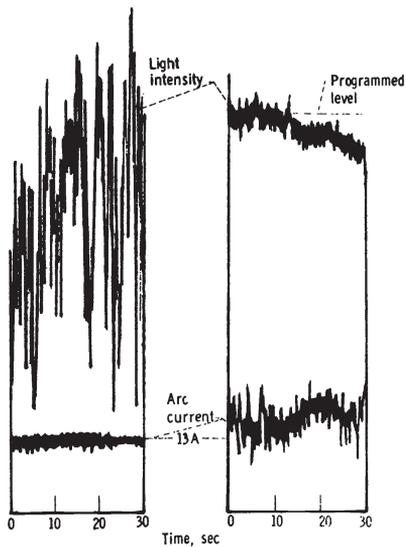


Fig. 3 Gordon arc
(a) Vaporization
at constant
current
(Courtesy author)

(b) Vaporization by
controlled
light intensity
(69)

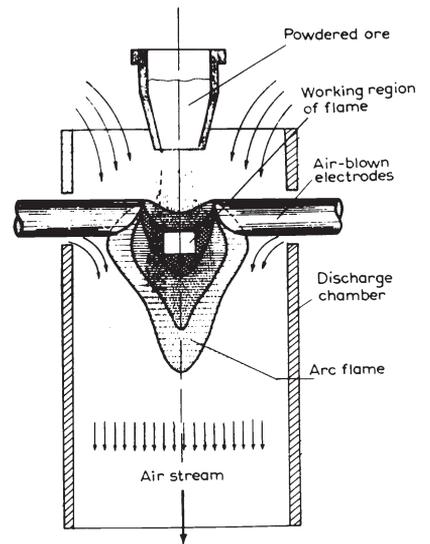


Fig. 4 Method of introducing
powdered ore into the
arc in a stream of air (10)
(Courtesy author)

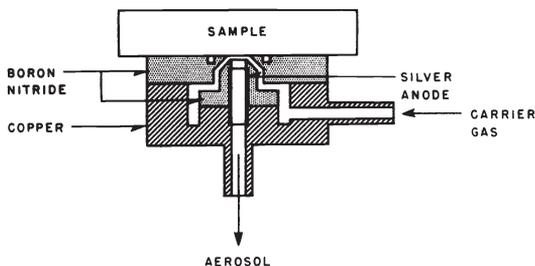


Fig. 5 Aerosol generator (11)
(Courtesy author)



Fig. 6 Hand held aerosol
generator for remote
analysis

In the liquid layer, solid sample, spark technique (15) strong evaporation of sample material is enforced, leading to a significant reduction in matrix effects. In addition, calibration can easily be accomplished via the composition of the spray liquid. Recently this method has been successfully used for the analysis of non-metallic samples prepared as metal pellets (16).

Discharges under reduced pressure. These discharges, especially hollow cathode discharges, have also been known for a long time but have not found widespread application. They are, however, very useful for trace analysis and for the determination of elements having analytical lines of high excitation potential, e.g. the gases and the rare gases, Cl, Br, I, S, C, Te, Se, As. Methods of more general application have been worked out lately (17).

Abnormal and obstructed glow discharges offer some new and very promising properties (Fig. 7). In the Grimm glow discharge lamp (18) sample material is removed layer by layer from the cold surface by cathode sputtering (Fig. 8) and excited in a low pressure discharge resulting in high precision and in almost complete absence of matrix effects.

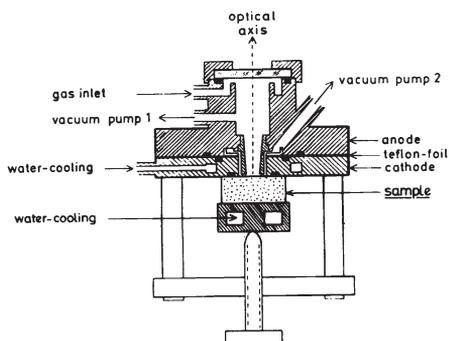


Fig. 7 Grimm glow discharge lamp



100 μm

Fig. 8 Scanning electron microscope photograph of Cu-surface after sputtering in glow discharge

Fig. 10 shows the surface of a copper powder pellet after sputtering.

The power of detection is comparable to that of DC-arc methods used for powder analysis in mineralogy and geochemistry and is demonstrated in Table 2. The precision is comparable with that of standard X-ray fluorescence methods (Table 3), but it may depend appreciably on the actual sample in question. Calibration is easy and can be done with the help of synthetic standards made up from oxides etc. A universal method permitting high precision and accuracy for a large variety of powdered materials is thus feasible (29).

With homogeneous samples the radiation output is constant with time. On the other hand, the layer by layer removal of material makes the method suitable for the in-depth analysis of surfaces, e.g. for corrosion studies (19-22). Resolution in-depth in the order of 100 nm can be obtained. Metals can be analysed directly if a sample is homogeneous and has a fine grain structure. Otherwise pellets made from filings or drillings must be used. The power of detection is comparable to that of high or low voltage spark methods (23). The precision is at least as good as with the latter method. Matrix effects, if any, are small. There-

fore, calibration is very simple and straightforward, e.g. materials as different as electrolytic copper, brass and bronze can be analysed with the same set of analytical curves or aluminium alloys can be analysed with one set of calibration curves independent of the type of alloy. Fig. 9 shows an example.

High precision analysis of gold has been reported (24) as well as routine analysis of steel and cast iron (25). Table 1 shows typical results for high alloy steel (26).

Non-metallic samples are analysed as compressed graphite (27) or preferably metal powder pellets (28).

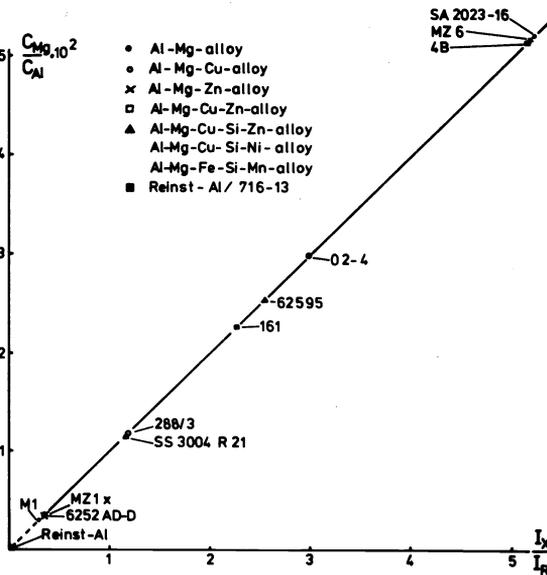


Fig. 9 Mg-determination in Al-alloys using a glow-discharge lamp

TABLE 1. The analysis of high alloy steel using the Grimm glow discharge lamp (26)

Element	Line [Å]	Weight concentration (%)	Standard deviation (+)	Relative standard deviation (+)
Ni	3461	20-40	0.28	0.7
Cr	4254	0.01-20	0.086	0.5
Fe	2599	5-50	0.39	0.8
Co	3502	0.01-45	0.48	1.0
Mo	3864	4-10	0.07	0.7
W	4302	0.01-5	0.02	0.4
Ti	4533	0.01-1	0.01	1.0
Mn	4033	0.1-1	0.007	0.7
Si	2881	0.2-0.6	0.004	0.7
Be	2348	0.2-0.8	0.003	0.5
C	1651	0.02	0.0003	1.3
S	1807	0.007	0.00004	0.6

(+) Referred to the highest concentration

cross excitation similar to that in a hollow cathode high intensity lamp (Fig. 11) (33).

An interesting new technique for the analysis of surfaces has recently been reported (34,35), which in some way is related to the glow discharge method. It makes use of the radiation emitted by the excited atoms which leave the surface as a result of an ion bombardment in high vacuum. Fig. 21 shows the experimental set-up, taken from (35).

LASER

Laser is a non-electric radiation source. Therefore, electrically conducting, as well as electrically non-conducting materials, can be analysed directly. The method is by now well known and the subject of a book (36) and comprehensive reports (e.g. 37). The application possibilities comprise local analysis with a spatial resolution of 10 - 20 μm , micro analysis and representative analysis of macro samples with little matrix effects (Fig. 12) (38) and high precision, if a number of shots are superimposed (39).

There are, however, two restrictions which should be mentioned, e.g.

The radiation output is lower than that of other sources, therefore requiring longer exposure times if used with spectrographic equipment. No such limitation will be experienced with photo-electric apparatuses.

The sample consumption is rather low, of the order of 0.3 mg/min with customary equipment. This may limit the determination of traces in heterogeneous powders (30,31) because of possible large signal fluctuations due to the small number of grains. The guarantee of purity may be much higher than the formally determined limit of detection (see Table 2, last column).

The precision at medium or low concentrations may then also be lower than with homogeneous samples. These are the same limitations as known with X-ray fluorescence methods. Under such circumstances it may be necessary to homogenize the material prior to analysis by fusing.

Contrary to most other excitation sources the spectroscopically more uncommon elements, mentioned above can be determined in the same way as all other elements if their analytical lines in the vacuum ultra violet region between 1100 and 2000 Å are used. Working gases having a higher ionisation potential than argon, enable the determination of Br, Cl, F, I, S, Se, As and Te with the help of analytical lines of high excitation potential in the visible region of the spectrum (32). The power of detection of glow discharge methods can be improved by an additional



10 μm

Fig. 10 SEM-photograph of powder-pellet after sputtering in glow discharge

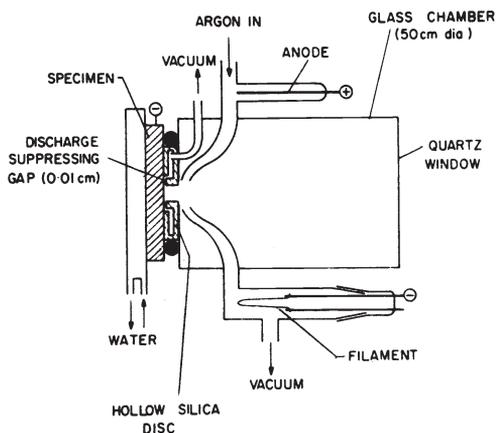


Fig. 11 Schematic diagram of the glow-discharge emission source with secondary-discharge electrodes (Courtesy authors) (33)

TABLE 2. Determination of traces in rocks and minerals using the Grimm glow discharge lamp

Spectrograph: 3.4 m Ebert, 1200/mm Grating
 Excitation: Burning voltage 1000 V, Current 130 mA, Argon pressure 10 mbar, Preglow 2 min.

Element	Line	\underline{c} (%) (+) $s_e = 50 \mu\text{m}$	\underline{c} (%) $\hat{s} = 1.5 \hat{R} = 2$	t (min)	\underline{c}_∞ (%)	\underline{n} Number of grains at limit of detection \underline{c}
Al	3962	$1.2 \cdot 10^{-4}$	$4.5 \cdot 10^{-5}$	20	$3.4 \cdot 10^{-5}$	1
Be	3321	$1.6 \cdot 10^{-4}$	$7.2 \cdot 10^{-5}$	43	$5.5 \cdot 10^{-5}$	1.4
Co	3454	$1.0 \cdot 10^{-4}$	$5.3 \cdot 10^{-5}$	60	$3.9 \cdot 10^{-5}$	0.44
Cr	4254	$4.4 \cdot 10^{-5}$	$1.2 \cdot 10^{-5}$	95	$9.2 \cdot 10^{-6}$	0.22
Ga	4172	$2.8 \cdot 10^{-5}$	$7.8 \cdot 10^{-6}$	64	$6.0 \cdot 10^{-6}$	0.12
In	4102	$3.3 \cdot 10^{-4}$	$1.6 \cdot 10^{-4}$	20	$1.2 \cdot 10^{-4}$	1.3
Mg	2852	$2.9 \cdot 10^{-4}$	$7.1 \cdot 10^{-5}$	142	$5.2 \cdot 10^{-5}$	1.3
Mo	3798	$1.6 \cdot 10^{-4}$	$3.5 \cdot 10^{-5}$	118	$2.6 \cdot 10^{-5}$	0.9
Ni	3415	$1.2 \cdot 10^{-4}$	$3.1 \cdot 10^{-5}$	86	$2.3 \cdot 10^{-5}$	0.5
Sr	4215	$2.7 \cdot 10^{-5}$	$7.3 \cdot 10^{-6}$	36	$5.5 \cdot 10^{-6}$	0.12
Ti	3653	$3.1 \cdot 10^{-4}$	$8.0 \cdot 10^{-5}$	111	$6.0 \cdot 10^{-5}$	1.7
Zr	3601	$2.6 \cdot 10^{-4}$	$5.1 \cdot 10^{-5}$	121	$3.8 \cdot 10^{-5}$	1.2

(+) $R_0 = 120\ 000$, $t = 20$ min

It is necessary to provide some kind of additional excitation of the laser produced vapour plume if high power of detection is desired. Spark source cross-excitation provides a simple means but other methods, e.g. microwave excitation (Fig. 13) (40) may offer definite advantages.

The full possibilities of laser OBS have not yet been fully explored. The possibility of sampling reproducibly small amounts is a rather unique feature and should encourage further efforts. The rather slow introduction of laser into the analytical practice may be due to the fact that available commercial apparatuses are rather built for one purpose only, i.e. local analysis and do

not easily provide for other modes of operation (41), Table 4. Nevertheless, fast semi-quantitative methods for the analysis of non-metallic samples including powders should find wide-spread application. Fig. 14 shows a set-up which is being successfully used for the direct analysis of cement raw materials (42).

TABLE 3. Determination of major constituents in rock samples using the Grimm glow discharge lamp
Spectrometer: ARL Quantometer 33000 Quantovac
Excitation: Burning voltage 1000 V, Current 130 mA, Argon pressure 10 mbar, Preglow 2 min, Integration time 20 sec.

Element	Conc.	s _{rel.} (%)	Sample	Element	Conc.	s _{rel.} (%)	Sample
Si 2216	24.5%	2.00	NIM-N	Mn 4034	0.13%	2.4	NIM-N
Si 2516	24.5%	0.65	NIM-N	Ti 3361	0.11%	6.4	NIM-N
Al 2575	8.8%	1.03	NIM-N	P 1775	0.03%	4.5	NIM-L
Fe 2382	6.3%	0.7	NIM-N	Cr 3594	0.29%	1.5	NIM-D
Mg 2791	4.5%	0.8	NIM-N	Ni 3619	0.21%	1.44	NIM-D
Ca 3007	8.3%	1.17	NIM-N	Zr 3438	1.28%	1.62	NIM-L
Na 3302	1.8%	7.6	NIM-N	Sr 4078	0.028%	1.9	NIM-L

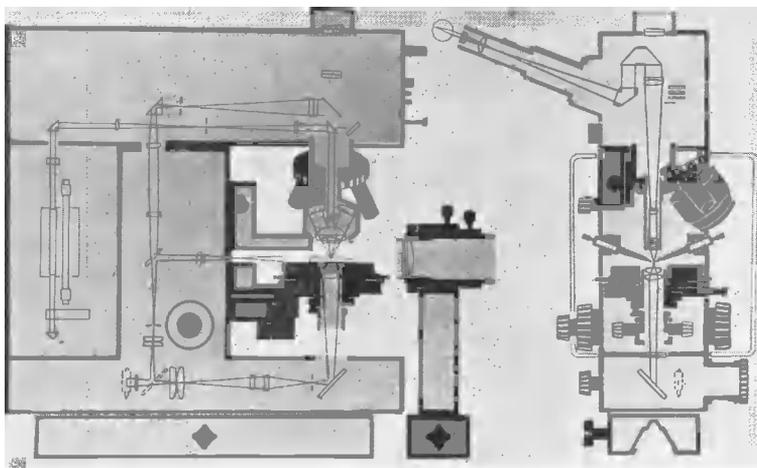


Fig. 12 LMA 10, Zeiss Jena
(Courtesy authors)

Of the many other radiation sources two useful for special purposes may be mentioned:

1. Microwave cavity discharges have been successfully employed for the analysis of micro samples especially with separate evaporation of the sample (Fig.15)(43). Excellent absolute power of detection has been reported. Such devices can also be used as specific detectors in gas-chromatography (44).

2. Exploding wire and exploding foil techniques offer another promising possibility for micro analysis (45,46).

SPECTRAL DISPERSION

Ebert, Ebert-Fastie and Czerny-Turner mountings of plane gratings are the most generally used spectral apparatus. Concave gratings are restricted to multi-channel photo-electric spectrometers especially with those having an extended spectral range (vacuum ultra violet). Excellent replicas of ruled gratings as well as of holographic gratings are available. With instruments of high resolving power low limits of detection can be obtained (47). Due to the grain of the photographic emulsion which determines the precision of the intensity measurement for photographic radiation measurement, not only high resolving power but high dispersion as well, is necessary in order to secure a sufficiently large measuring area for spectrum line photometry. As a consequence these instruments are rather large. Photo-electric spectrometers with a number of separate output channels derived from corresponding exit slits in the focal plane of the spectrometer must also have high dispersion because of the finite size of the slits. The increased use of radiation sources constant in time, e.g. flames, plasmas, low pressure discharges had

led to the development of spectral instruments operating sequentially. However, for trace analysis they should allow the simultaneous measurement of the spectral background (48). Computer controlled high resolution step motors enable the construction of versatile monochromators which can easily be adapted to changing analytical needs and offer greater flexibility than polychromators (49), but perhaps at the expense of some loss of precision. The introduction of two-dimensional photo-electric radiation detectors into OES has fostered the development of echelle spectrometers, in which dispersion in two directions perpendicular to each other results in a two-dimensional spectrum.

With the latter photo-electric measuring devices it is the resolving power of the apparatus which matters whereas the linear dispersion is of secondary importance. Therefore, these spectrometers can be built small and compact to the advantage of thermal and mechanical stability. Focal lengths of 20 to 50 cm are common.

TABLE 4. Variation of intensity ratios with matrix in laser probe spectra (41)

Element	Spectral line (\AA)	Intensity ratios				Coefficient of variation (%)
		BaF ₂	Al ₂ O ₃	Yb ₂ O ₃	WO ₃	
Co I	2587.2	0.46	0.61	0.54	0.56	11
Cr II	2766.5	1.30	1.28	1.23	1.38	5
Cr II	3124.9	1.49	1.57	1.49	1.43	4
Fe II	2599.4	1.89	1.89	1.57	1.59	10
Fe II	2611.8	1.20	1.13	0.99	0.99	10
Mn II	2933.0	2.32	2.09	2.01	2.15	6
Mn II	3441.9	1.44	1.47	1.61	1.64	6
Fe I	3021.0	1.00	0.81	0.98	0.75	14
Mn I	3228.0	1.30	1.05	1.05		13
Mo I	3170.3	1.44	1.23	1.05		16
Ni I	3437.2	1.85	1.75	1.58		8

distribution of the electrical field strength

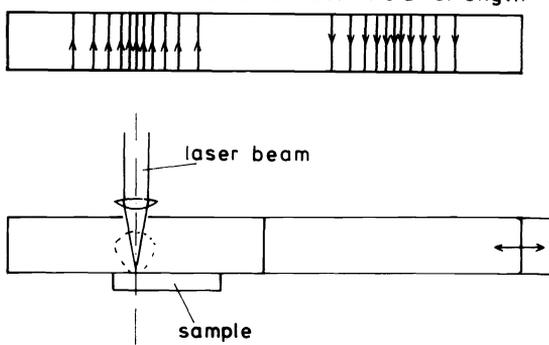


Fig. 13 Microwave excitation of laser-produced vapour plume Resonant cavity (H_{102})

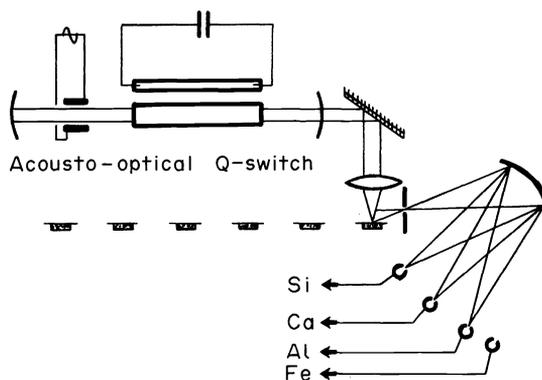


Fig. 14 Direct reading spectrochemical analysis of cement raw material using laser excitation (Courtesy authors) (42)

RADIATION DETECTORS

The photographic emulsion has some unique properties, e.g.

1. It is a two-dimensional radiation receiver permitting spatial as well as intensity discrimination.

2. It has an almost unlimited integration capability.
3. High inherent amplification, i.e. only a few radiation quanta make a silver halide grain of about $1\frac{2}{3}$ μm developable.
4. A photographic record can be stored indefinitely and re-examined at will. Its information capacity is unsurpassed.
5. Background intensity measurements as afforded in trace analysis can easily be made.

Therefore, the photographic emulsion is still at least equivalent to other methods as regards power of detection as long as the available amount of sample is unlimited, whereas, with limited sample amount, photo-electric devices can be much superior. Against these virtues must be put the following disadvantages:

1. Processing and evaluating affords much time and highly skilled personnel. Therefore, speed and throughput of samples is rather limited.
2. The obtainable precision is only 3 - 5%.

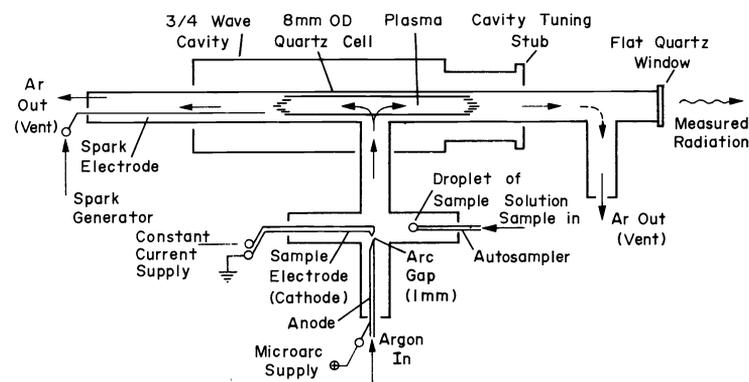


Fig. 15 Microwave excitation of small samples
Microarc and plasma cell, showing the
microarc electrode configuration
(Courtesy authors) (43)

Understandably efforts have been made to overcome some of the drawbacks. Improvement is possible in two ways:

1. The photographic plate is measured as customary with a spectrum line photometer but the time consuming and tedious calculations afterwards are performed with the help of a computer. In this way extensive calculation and correction procedures can be used and more information can be taken into account for the actual analysis (50,51,52). On a smaller scale such calculations can be done on some of the new programmable pocket or desk calculators. The instructive but slow and cumbersome calculating boards are a thing of the past.
2. Much more time and manpower can be saved, and more information contained on the photographic emulsion taken into account, if the manual photometry is replaced by automatic photometry using a programmable recording photometer with automatic transfer of data into a computer (53 - 57). With such a combination the complete time for measuring and evaluating a plate with 20 spectra can be as short as 30 min. A revival of photographic analysis procedures is thus possible. Unfortunately, the complete equipment is then rather expensive and therefore such methods have to compete with some of the new photo-electric methods.

Photo-electric radiation detectors. In OES the radiation flux through the spectrometer is usually of such a strength that even with limited amounts of sample a large number of quanta are available for intensity measurement. Therefore, with photomultiplier tubes the relevant source of noise is signal noise. Consequently, time multiplexing methods offer little advantage, if any. Almost the same applies to photon counting.

Photo-electric intensity measurement is either done in connection with a monochromator, i.e. in a single channel sequential mode or with a polychromator. In the latter case true simultaneous measurement which is much better suited to multi-element analysis is accomplished. Because of the rather limited number of signal channels such methods are restricted to routine analyses of similar samples. The sample throughput can be very high.

New developments offer promising extensions of the photo-electric measuring techniques, which eventually may lead to procedures combining the high informa-

tion capacity of the photographic emulsion with the precision, dynamic range and speed of the photo-electric detectors: (58,59).

Linear silicon photodiode arrays (Fig. 16).

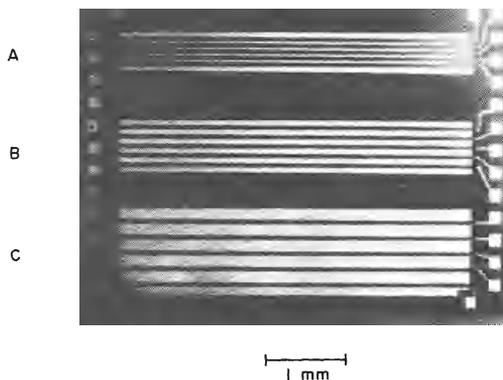


Fig. 16 Linear silicon photodiode arrays
 Length: 3 mm
 Width of diode strip: 20 μm
 Space between diodes: A 25 μm ,
 B 50 μm , C 100 μm
 (Diodes appear dark)
 (Courtesy authors and publisher)(60)

These arrays consist of a series of diode strips as small as 25 μm and with spacings of the same magnitude. The diodes have a high quantum efficiency over the whole ultra violet and visible spectrum range. Unfortunately, they have not the almost noise-free internal amplification of the photomultiplier and therefore must be operated in combination with low noise pre-amplifiers. Two methods of operation are being investigated:

In the first mode of operation a large number of diodes, up to 1000 and more, are positioned in the focal plane of a spectrometer, the dispersion of which is chosen in such a way that the desired part of the spectrum is matched to the physical length of the array which may be about 25 mm long. The readout is done

sequentially. There are versions which allow integration and consequently simultaneous measurement of intensities (61).

The other method makes use of a comparatively small number of diodes each being connected to external, carefully matched low noise amplifiers. With such arrays it is possible to measure simultaneously on several channels within a small part of the spectrum, e.g. analytical line and adjacent background. The main advantages of such systems are the following: high quantum efficiency, high stability, no drift, no fatigue, large dynamic range, excellent linearity. As compared to photomultiplier tubes they are better in the visible spectrum range whereas the latter are better in the ultra violet. Because of the rapid development in this field, they may soon replace photomultiplier tubes for many applications. One example for an analytical application is shown in Fig. 17 (62).

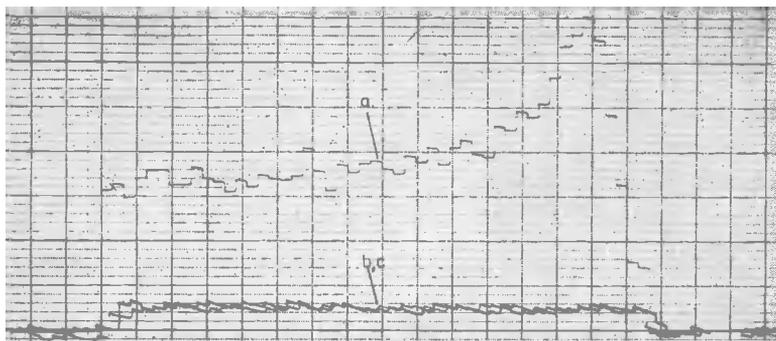


Fig. 17 Linear silicon photodiode array as radiation detector in spark analysis of aluminium. Intensity versus time curves for a) Cu 3274 \AA and b,c) background (5 x magnified). Each step corresponds to a micro-integration of 40 sparks

Regarding two-dimensional photo-electric radiation detectors in spectrochemical analysis, basically two different approaches can be distinguished:

1. An echelle spectrum is produced on the photocathode of an image dissection tube (sometimes after amplification or wavelength conversion by an image identifier tube) and sequentially measured. Basically this tube is a photomultiplier tube with an externally positionable, very small, effective part of

the photocathode. It therefore has all the advantages of such a system: very low dark current because of the small cathode, large dynamic range, high sensitivity, high internal low-noise amplification. It is possible to count single photons. The electrical signals obtained by sequential readout (usually done in a random access mode) are transferred into a computer and there suitably evaluated (63). A complete computer integrated system has recently become commercially available (Fig. 18). It is best suited for radiation sources stable in time, e.g. flames, plasmas, glow discharges. Such systems apparently are extremely versatile and should find many applications.

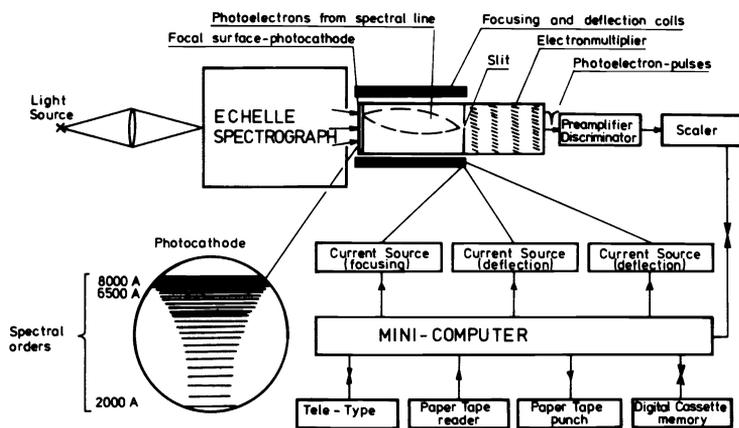


Fig. 18 Image dissection echelle spectrometer (Reproduced from a prospectus of the manufacturer Scandia AB)

respectively (which however presents some difficulties) (57,64,65). The readout signals are stored in a computer and again suitably evaluated. These systems offer true simultaneous measurement and therefore multi-element facilities similar to those with photo emulsions. (One such system is known under the trade name OMA, i.e. Optical Multi-channel Analyzer). A number of instruments, mostly in combination with vidicon camera tubes of different properties have been described recently. Much better use of TV camera tubes can be made if again an echelle spectrometer is used. A complete computer-controlled instrument having a resolution of 1000 by 1000 pixels (picture elements) has recently been described (Fig. 19) (66).

2. Television camera type detectors.

A number of systems have been described in which part of the spectrum produced by a customary spectral instrument is projected onto the light sensitive photoconductor or dielectric-storage layer of such a detector tube. The optical image is first transduced into an analogous electrical charge pattern which may be integrated over some time and then finally read out sequentially, either by raster or by random access scanning

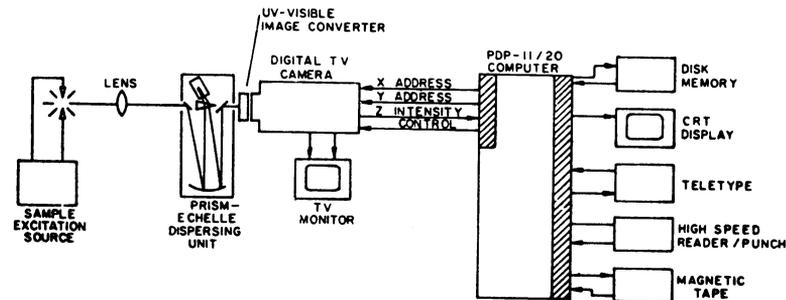


Fig. 19 Block diagram of computerized TV emission spectrograph

Unfortunately, until now these instruments suffer from a number of disadvantages: appreciable noise, no linear transfer characteristics, low dynamic range. Silicon vidicons with a two-dimensional array of discrete photodiodes offer an already better performance than most other types of television camera tubes, which after all are designed and built for quite different purposes. Tubes designed and constructed for use in

spectroscopy could yield much better results. In the immediate future significant improvements can be expected and consequently instruments which could replace customary photographic spectrographs.

CONCLUSION

Finally a technique should be mentioned which is somewhat out of the normal way but which for special applications offers great simplicity of instrumentation, i.e. the use of resonance fluorescence detectors (67). Suitably modulated in connection with one of the stable excitation sources very compact single or multichannel spectrometers can be constructed without any dispersing element (68,70). The principle of such a system is shown in Figure 20.

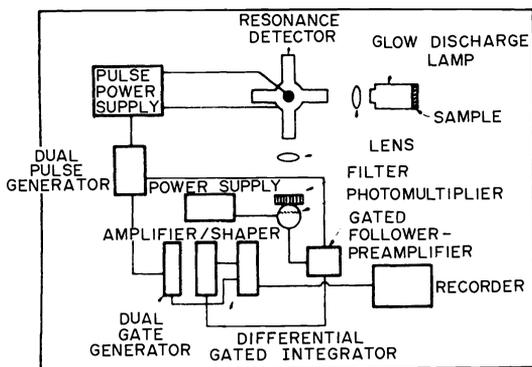


Fig. 20 Dual-gated integration resonance fluorescence detector system (Courtesy authors)

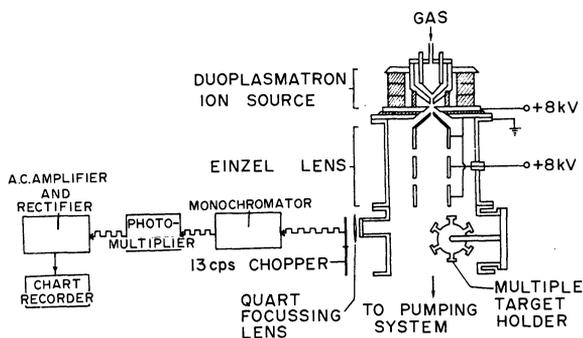


Fig. 21 Schematic diagram of the IBSCA (Ion-beam sputtering spectrochemical analysis) apparatus (Courtesy authors) (35)

To conclude, it is hoped that this survey has shown the rather exciting progress which is being made in all fields of OES. As he was in the past the analyst will in the future remain in a position to cope successfully with new challenges.

REFERENCES

1. Ch.E. Harvey, Semi-quantitative Spectrochemistry, Appl. Res. Lab. Glendale, California, (1964).
2. J. Kroonen and D. Vader, Line Interference in Emission Spectrographic Analysis, Elsevier, Amsterdam (1963).
3. A.J. Mitteldorf and D.O. Landon, Appl. Spectrosc. **10**, 12-27 (1956).
4. P.W.J.M. Boumans, Spectrochim. Acta **31B**, 179-199 (1976).
5. R. Avni, H. Harel and I.B. Brenner, Appl. Spectrosc. **26**, 641-645 (1972).
6. I.B. Brenner, H. Eldad, L. Argov, A. Harel and M. Assons, Appl. Spectrosc. **29**, 82-85 (1975).
7. A.F. Dorrzapf, Jour. Research U.S. Geol. Survey **1**, No. 5, 559-562 (1973).
8. V. Vukanović, V. Georgijević, N. Kujević and D. Vukanović, Proc. XII Coll. Spectr. Int., Exeter, 193-198 (1965), Hilger, London (1965).
9. D. Lummerzheim, Dissertation TH Aachen, Jül-614-RW (1969).
10. A.K. Rusanov and T.J. Tarasov, Shurn. analit. chim. **10**, 267 (1955).
11. J.L. Jones, R.L. Dahlquist and R.E. Hoyt, Appl. Spectrosc. **25**, 628-635 (1971).
12. K.H. Koch and K. Ohls, Spectrochim. Acta **23 B**, 427-433 (1968).
13. P. Höller, Ch. Thoma and U. Brost, Spectrochim. Acta **27B**, 365-375 (1972).
14. K. Slickers, E. Wild and E. Hoffmann, Aluminium **50**, 588-591 (1974).
15. R.M. Barnes and H.V. Malmstadt, Anal. Chem. **46**, 66-72 (1974).
16. K. Ohls, private communication.
17. K. Thornton, Analyst **94**, 958-967 (1969).
18. W. Grimm, Spectrochim. Acta **23B**, 443-454 (1968).
19. C.J. Belle and J.D. Johnson, Appl. Spectrosc. **27**, 118-124 (1973).
20. H. Schneider and H. Schumann, Kernforschungszentrum Karlsruhe, KFK 2009, July 1974.
21. R. Berneron, Proc. Coll. Spectr. Int. XVIII, Grenoble, I, 263-267, Paris 1975.
22. G. Baudin, Centre d'Etudes Nucléaires de Saclay, Conférence CEA-CONF-82, May 1976.
23. M. Dogan, K. Laqua and H. Massmann, Spectrochim. Acta **27B**, 65-88 (1972).
24. H. Jäger, Anal. Chim. Acta **58**, 57-64 (1972).
25. H.W. Radmacher and M.C. de Swardt, Spectrochim. Acta **30B**, 353-360 (1975).
26. H. Grimm, private communication.

27. M.E. Ropert, C.R. Acad. Sc. Paris 271, Series C, 992 (1970).
28. J.Y. Moal, G. Brossier, Coll. Spectrosc. Int. XVI, Heidelberg, II, 219-226 (1971).
29. S. El Alfy, K. Laqua and H. Massmann, Z. Anal. Chem. 263, 1-14 (1973).
30. A.D. Wilson, Analyst 89, 18-30 (1964).
31. C.O. Ingamells and P. Switzer, Talanta 20, 547-568 (1973).
32. I. Kenawy and K. Laqua, unpublished.
33. R.M. Lowe, Spectrochim. Acta 31B, 257-261 (1976).
34. N.H. Tolck, 5th Int. Conf. on Atomic Spectrosc., Melbourne 1975, Book of Abstracts.
35. I.S.T. Tsong and A.G. McLaren, Spectrochim. Acta 30B, 343-351 (1975).
36. H. Moenke and L. Moenke, Laser Micro-Spectrochemical Analysis, Hilger, London (1973).
37. A. Felske, W.-D. Hagenah and K. Laqua, Naturw. 57, 428-434 (1970).
38. L. Moenke-Blankenburg, H. Moenke, K. Wiegand, W. Quillfeldt, J. Mohr, W. Grassme, Jenaer Rundschau 3, 107-111 (1975).
39. A. Felske, Dissertation, Univ. Münster (1969).
40. F. Leis, Dissertation, Univ. Düsseldorf (1976).
41. A.B. Whitehead and H.H. Heady, Appl. Spectrosc. 22, 7-12 (1968).
42. J.P. Méric and J.F. Caron, Coll. Spectrosc. Int. XVII, Florence, II, 503-507 (1973).
43. L.R. Layman and G.M. Hieftje, Anal. Chem. 47, 194-202 (1975).
44. K. Durrant and R.H. Tyas, Coll. Spectrosc. Int. XVII, Florence, III, 165-169 (1973).
45. R.D. Sacks and C.S. Ling, Anal. Chem. 47, 2074-2081 (1975).
46. C. Triché, Dissertation, Univ. Toulouse (1971).
47. K. Laqua, W.-D. Hagenah and H. Waechter, Z. Anal. Chem. 225, 142-174 (1967).
48. M. Nordmeyer, Spectrochim. Acta 27B, 377-383 (1972).
49. R.W. Spillmann and H.V. Malmstadt, Anal. Chem. 48, 303-311 (1976).
50. M. Margoshes and S.D. Rasberry, Spectrochim. Acta 24B, 497-513 (1969).
51. R.J. Decker and D.J. Eve, Spectrochim. Acta 25B, 479-486 (1970).
52. J.A. Holcombe, D.W. Brinkmann and R.D. Sacks, Anal. Chem. 47, 441 (1975).
53. F.G. Walthall, J. Res. U.S. Geol. Survey 2, 61-71 (1974).
54. A.W. Witmer, J.A.J. Jansen, G.H. van Gool and G. Brouwer, Philips techn. Rdsch. 34, 325-333 (1974/75).
55. O. Beuck, W.-D. Hagenah and K. Laqua, Coll. Spectrosc. Int., Florence, I. 258-261 (1973).
56. A.W. Helz, J. Res. U.S. Geol. Survey I/4, 475-482 (1973).
57. M. Margoshes, Spectrochim. Acta 25B, 113-122 (1970).
58. Y. Talmi, Anal. Chem. 47, 1510-1516 (1975).
59. Y. Talmi, Anal. Chem. 47, 658-670 (1975).
60. P.W.J.M. Boumans, R.F. Rumphorst, L. Willemsen and F.J. de Boer, Spectrochim. Acta 28B, 227-240 (1973).
61. G. Horlick, Appl. Spectros. 30, 113-123 (1976).
62. H. Bubert and W.-D. Hagenah, 11. Spektrometertagung, Montreux, 9(1976).
63. A. Danielsson and P. Lundblom, Appl. Spectrosc. 30, 151-155 (1976).
64. T.A. Nieman and C.G. Enke, Anal. Chem. 48, 619-624 (1976).
65. J.D. Ganječ, N.G. Howell, J.R. Roth and G.H. Morrison, Anal. Chem. 48, 505-510 (1976).
66. D.L. Wood, A.B. Dargis and D.L. Nash, Appl. Spectrosc. 29, 310-315 (1975).
67. J.V. Sullivan and A. Walsh, Spectrochim. Acta 22, 1843-1852 (1966).
68. L.R.P. Butler and C.D. West, 5th Int. Conf. on Atomic Spectrosc., Melbourne 1975, Book of Abstracts.
69. W.A. Gordon, NASA TN D-4236 (1967).
70. L.R.P. Butler, K. Kröger and C.W. West, Spectrochim. Acta 30B, 489-499 (1976).