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First Italo-Hungarian Symposium on Spectrochemistry: Environmental Protection and Spectrochemistry

Proceedings by:
S. Caroli, A. Alimonti and F. Petrucci

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FIRST ITALO–HUNGARIAN SYMPOSIUM
ON SPECTROCHEMISTRY:
ENVIRONMENTAL PROTECTION AND SPECTROCHEMISTRY

Istituto Superiore di Sanità
Rome, 5 – 9 September 1983

Proceedings by
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FIRST ITALO-HUNGARIAN SYMPOSIUM ON SPECTROCHEMISTRY: ENVIRONMENTAL PROTECTION AND SPECTROCHEMISTRY

Istituto Superiore di Sanità, Rome, Italy, 5-9 September 1983
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The first Italo–Hungarian Symposium on Spectrochemistry was held in Rome on 5–9 September 1983, and was devoted to the fascinating theme of the applicability of spectroscopic techniques for protecting environment and human health and welfare. The meeting, organized by the Istituto Superiore di Sanità with the support of the Italian Foreign Office and National Council of Research as well as the Hungarian International Institute of Culture and the J. Eötvös University of Budapest, aimed at outlining the significant contributions made so far by the two countries within the framework of their scientific cooperation programmes on spectrochemical research. At the same time emphasis was laid on the increasing importance gained over these last years by spectroscopy in general for environmental protection. The spectrochemist attending conference thus had a survey of the many possibilities offered by modern spectroscopic techniques in this limitless application area.

Nineteen plenary lectures, delivered by distinguished spectroscopists, formed the body of the scientific programme of the Symposium. Throughout the week of the conference the different facets of emission and absorption atomic spectroscopy, X–ray spectrometry, gas–mass spectrometry, neutron activation analysis, Raman spectroscopy and various laser–based methodologies were discussed in detail. The participants were provided with the overall impression of how rapidly and efficacious these techniques are expanding their capabilities for environmental uses. This volume also contains the discussions of the two round–table sessions. They covered the problems of analytical chemistry in environmental protection and development of spectrochemical methods for investigation of biological materials, and the entire audience was stimulated in an open debate.

One fact clearly emerged during the meeting, and that is the need for an ever closer collaboration between the spectroscopist practitioner and the life scientist in order to adequately face the tremendous analytical problems of today. Revival of interest in emission spectroscopy, especially consequent to the development of the inductively–coupled plasma and low–pressure sputtering sources, was also noticeable. Nor was forgotten the role played by spectrochemistry in establishing and implementing national and international regulations.

As a collective effort, the success of the Symposium should be acknowledged to all participants, to whom we express our sincere gratitude. A particular word of thanks is addressed to the EEC Joint Research Centre of Ispra for organizing an exciting three–day post–conference tour of the Establishment laboratories.

It is hoped that through this volume the reader will have the perception of the mutual attitude which marked the symposium, i.e. that of a fruitful collaboration of a variety of specialists for achieving a common and rewarding objective.

S. CAROLI and K. ZIMMER

Chairmen of the Symposium
OPENING ADDRESSES

Welcome by F. MERÉNYI, Director of the Hungarian Academy in Rome

Ladies and Gentlemen, dear Friends!

It is my privilege to welcome you here in the Hungarian Academy of Rome, on the occasion of the opening of the First Italo-Hungarian Symposium on Spectrochemistry. The cultural relationships between our two countries have always yielded generous fruits, with mutual enrichment, as testified by an endless sequence of past and recent events.

Man, his necessities and his harmonious development have been constantly in the focus of our common efforts to preserve and steadily improve the quality of life in a variety of humanistic and scientific respects. In this framework the scientific programmes jointly carried out by Italy and Hungary play an important role in as much as sanitary and environmental protection constitutes one of the topics more frequently underlining a great number of our research projects. Traditionally, a relevant part of these activities is managed by the Istituto Superiore di Sanità in cooperation with the main Hungarian academic institutions, such as the Eötvös Loránd University of Budapest.

The Symposium which starts today is a result of the significant progress made in this direction by both countries over the last few years. Devoted specifically to the many applications of spectrochemical techniques for environmental purposes, this first gathering is to be the initiator of a series to which we wish a long and prosperous life. Its theme is indeed suggestive and reflects the wide possibilities offered by modern methods of investigation.

On the one hand, the complex reality of our times and, on the other hand, the close interdependence of knowledge point out more and more clearly that man’s battle is to restore environment from the most severe damages preposterously caused in the past and guarantee future generations a world worth living in. This is certainly not an easy task and demands cooperative effort on a global scale. Many years will be necessary to evidence and consolidate the results of this awareness, but let us remember that Rome, which hosts our works, was not built in a day.

Anyway, since the shorter an official speech, the more appreciated, allow me, dear friends, to stop now and simply wish you all a successful week of fruitful discussions and exchange of viewpoints.

Buon lavoro a tutti. Eredményes munkát kívánok.

Introduction by F. POCCHIARI, Director General of the Istituto Superiore di Sanità, Rome, Italy

Ladies and Gentlemen, distinguished Guests!

It is a great pleasure for me to have the opportunity to open the First Italo-Hungarian Symposium on Spectrochemistry in this magnificent building Palazzo Falconieri.

The theme to be discussed is one of today’s most stimulating subjects and its felicitous timeliness should be acknowledged.

In fact, the potential of modern instrumental techniques of investigation for health protection in general and control and monitoring of environmental pollution in particular has become quite something over the last decade. This might in turn pose a very fundamental question on whether it is our environment that is getting more and more polluted, or it is only the improvement of analytical procedures to face present problems that makes it seems so. A debate on this point could be quite fascinating. The net result of this situation, however, is that legislation updates progressively to meet the capability of testing methods which can detect ever smaller traces of chemicals as requirements become more and more stringent.

Spectrochemical methods, intended in a broad sense, take the lion’s share to date because of the wide possibilities they have to determine pollutants in a variety of environmental and biological samples. They provide a major contribution in establishing both maximum and average levels, thus realizing a highly valuable integration of both the regulatory and scientific aspects, expediently finalised to the overall goal of protecting man and his environment.

Research programmes performed by our two countries insofar as application of old and newly developed spectroscopic procedures in the said field is concerned have originated a wealth of information and experimental data which strongly support the validity of this prospect.

This Symposium will highlight the most significant progresses made by Hungary and Italy, jointly and singly, in this area.

I trust all our participants will find the discussions pleasant and productive and wish our Hungarian guests a very agreeable stay in Rome.
Ladies and Gentlemen, dear Colleagues and Friends!

The presentation of the Symposium made by Prof. Menéndez and Prof. Pocchiari has been so explicative that I was wondering whether anything else really essential could be added. But notwithstanding the sense of relief which I imagine would pervade the audience should I stop immediately and thus give place to the other more pleasant events of this evening, it seems to me that there are still two or three points which would deserve mention. We are all well aware of the fact that this last century has brought progressive deterioration to our environment as a consequence of industrial wastes, traffic, indiscriminate use of pesticides, etc. Serious health problems have thus ensued which nowadays demand an as early as possible detection and identification of noxious agents in practically all kinds of materials.

Continuing development and refinement of sensitive physico-chemical methodologies have paralleled and demonstrated the increasing severity of this contamination, which can be thus adequately faced in a sort of self-perpetuating challege. Spectroscopy, with its variations, which all however stem from and exploit the interaction of radiations with matter, lends itself most profitably to environmental and bioclinical studies. In the course of this Symposium not only the new applicative aspects of techniques already consolidated and regularly employed, but also theoretical and instrumental features of less popular though highly promising methods will be examined in detail.

In this connection it hardly needs to be recalled the importance of emission spectroscopy and its renaissance consequent to the discovery and widespread diffusion of new excitation sources such as the inductively-coupled plasma and low-pressure discharges. Simultaneous determination of elements is of immense value, especially when analyzing biological samples for which knowledge of the variations from normal levels for elements other than those directly concerned is mandatory for a correct interpretation of the phenomena under study.

On the other hand, atomic absorption spectrometry is probably still unsurpassed as a means for investigating pollution of fresh and marine waters. Relative simplicity of utilization requiring only brief training of personnel together with high detection power accounts for most of AAS’s success.

Monitoring of organic chemicals falls well within the province of mass spectrometry, especially when the last is coupled with gas chromatography. Furthermore, laser-based spectroscopic techniques are rapidly gaining importance for their wide capabilities in pollution control in the atmosphere.

This list however could go on forever: the merits of neutron activation analysis, Raman spectroscopy, X-ray diffraction and fluorescence spectrometry, or nuclear magnetic resonance are so well known that it would be useless even attempting to summarize them here.

The lectures to be delivered in the next few days and the exchange of ideas which will follow aim at outlining the most recent advances in the various methodologies as for health and environmental protection. The environmentalist can thus rely on one powerful weapon more in his arsenal.

This Symposium will provide a forum for both academic and industrial scientists to discuss their viewpoints and exchange their experiences. Moreover, it is also a due acknowledgment to the cooperative efforts carried out by our two countries in this field ever more efficaciously during these last years. The time was ripe for organizing this event, the first one of a series planned to take place regularly in order to present latest achievements, promote developments and stimulate even closer communication between Italy and Hungary.

But before I try your patience too much, I shall close rapidly expressing my gratitude to all those who have so actively and validly cooperated in organizing this meeting and to all of you for being here. Once again, thank you very much.

Development of the Italo-Hungarian cooperation in the field of spectrochemistry by K. ZIMMER, Eötvös Loránd Tudományegyetem, Budapest, Hungary

Dear Guests and Friends!

Let me start my welcoming address with a personal reminescence. It was 21 years ago that I first visited Rome as a scholar. I lived in the building where we are now. At that time the Director of the Hungarian Academy in Rome was the same Professor Ferenc Menéndez whom we now welcome here. As an appreciation of his fruitful activities, he was recently awarded the golden degree of the Order of Labour by our Presidential Council, for which I sincerely congratulate on behalf of all participants of this meeting.

At that time, I was working in the spectroanalytical laboratories of the Istituto Superiore di Sanità. There I met Professor Giulio Milazzo who dealt with spectroscopic research and retired some years ago as well as the late professors Intonti and Cotta-Ramusino. This was the origin of the connections between this Institute in Rome and the Institute
of Inorganic and Analytical Chemistry of the Lorand Eötvös University in Budapest. At the Istituto Superiore di Sanità, extensive research work was carried out on the field of hollow cathode analysis, both for the detection of impurities in pure substances and for the compilation of a spectrum atlas.

The mutual visits between the representatives of the two institutes started eleven years ago, when Dr. Sergio Caroli became an active participant of the research. Soon afterward a scientific cooperation began. This cooperation aimed at the elaboration and application of new spectrochemical methods for the trace analysis of biologically active samples based on the investigation of human organs, primarily brain. As we all know, these analyses have utmost importance in environmental and health protection. To mention only one example, the presence or absence or significant changes in the concentration level of certain trace elements may cause severe malfunctions in certain organs.

Hollow cathode excitation, with significant traditions in Rome, has created a new school. With the guidance of Professor Tibor Torok, academic research of similar nature had started in Budapest. Our Italian partner expressed his interest toward our results in the evaluation of spectra and our research on the spectrochemical analysis of trace metals in human organs. For a certain period, two departments of the Medical University of Budapest contributed to this work, and then Dr. Károly Florián of the Chemistry Department of the Technical High School of Košice (Czechoslovakia), whom we can also welcome here, joined our project enthusiastically.

The investigations have been extended to the surface analysis of semiconductors playing important role in the electronic and metal industry. These investigations are led by Dr. Gyula Záráy, head of the laboratory of Hungalu Engineering and Development Centre in Budapest, who is also present here.

Recently joined the project Dr. György Heltai, senior lecturer of the Chemical Department of the University for Agricultural Sciences of Gödöllő, with agrochemical and environmental research.

A proposal for the scientific collaboration between the two institutes was signed in November, 1975, then in February, 1977, the Hungaro–Italian Scientific and Technical Joint Commission approved the proposal and placed it on the scientific and technical schedule of the Governments of Italy and Hungary. The details of the collaboration were fixed by the two partners. The collaboration was extended to the development of methods for trace analysis, primarily with the aim of improving their performance, including the application of the up–to–date possibilities of programming offered by mathematical statistics.

As a direct continuation of the previous five–year plan period, the collaboration was extended to 1984, and in November 1982, the heads of the two institutes, Professor Francesco Pocchiari and Professor Ferenc Nagy signed the agreement of scientific collaboration for the years 1983 to 1987.

These fruitful connections have proved to be very useful, and permitted the first Italo–Hungarian Symposium on Spectrochemistry to be organized. The idea of this joint event was due to Professor Sergio Caroli, and it was he who has done the most in realizing this Symposium. Thanks are due for the organizing work to Dr. Giuliano Grazzioli of CNR, Professor Guglielmo Castro of the Italian Foreign Ministry, furthermore to the officials of the Hungarian Academy in Rome, primarily to Mr. János Knopp, and to the representative of the Institute of International Relationships present here, Mrs. Éva Rázzó. It was their enthusiastic work that made it possible for us to arrive at this Symposium now.
DEVELOPMENT OF A HOLLOW CATHODE METHOD FOR THE SPECTROANALYTICAL DETERMINATION OF TRACE ELEMENTS IN BIOLOGICAL MATERIALS

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Summary. — Direct determination of the elemental composition of samples in powder form, for example from the ashing of biological materials or from airborne dust samples, is very attractive as no undesirable excessive manipulation is required as is the case when digestion procedures are involved. In recent years spattering sources (mainly the Grimm’s glow discharge and the hollow cathode discharge) have manifested great potential in this field. Their atomization mechanism in fact allows sample material to be uniformly transported into the excitation zone, thus minimizing phenomena of selective volatilization. The hollow cathode discharge in particular offers a number of definitive advantages even over glow discharge. Many different procedures can be envisaged for the introduction of samples into the cathode cavity ranging from simply placing loose powder on the cathode bottom to pressing it with various binding materials to prepare pellets of different shapes (as hollow cylinders or disks) to be slipped into the cavity. Nature of samples and analytes as well as working conditions chosen to operate the discharge determine the form, composition and aggregation state most suited for optimizing the analytical procedure.

Introduction

Environmental control is taking more and more advantage of the enormous investigatory potential of spectroscopic techniques in general. Developments in analytical procedures and instrumental facilities keep pace bravely with the ever more stringent requirements set by international recommendations and national legislations.

Industrial effluents, agricultural pesticides and fuel combustion among others have severely polluted our environment during this century posing serious risks to human health and welfare. Potentially toxic agents in biological materials as well as in the environment require therefore to be identified as early as possible. Furthermore, modern trends in biocatalytic chemistry emphasize the necessity of performing simultaneous determinations of elements in biological fluids and tissues since only this approach can guarantee a realistic evaluation of the effects produced by variations from physiological levels for those elements specifically under study.

The last decade has also testified the increasing importance of determining trace and ultratrace elements essential for man, as vital functions may be seriously impaired by alterations in their equilibrium.

Within this framework, atomic spectroscopy plays a fundamental and well-consolidated role demonstrating an undeniable ability to lend itself to the correct interpretation and solution of the complex problems of detecting, quantifying and monitoring elements in all sorts of materials. Insofar as multielement determinations are concerned, atomic emission spectroscopy in
particular has been the object of deep, renewed interest in the recent past, mostly as a consequence of the introduction of new excitation sources or the revival of some whose applicability had been not sufficiently exploited for various reasons.

Analysis of solutions is in most cases well accomplished by two mutually integrating techniques, i.e. atomic absorption and inductively coupled plasma spectrometry. One major effort in this field at present aims at a reliable direct assay of liquid samples of a complex nature such as blood, urine and marine waters. The still unsurpassed detection power and relative ease of operation of the former technique are counterbalanced by the multielement capability and lower matrix dependence of the latter. This will be amply illustrated by the other lecturers.

The elemental composition of solid specimens at trace level in turn can be determined in emission spectroscopy essentially by either various excitation sources or even X-ray based techniques. In the first case an appreciable amount of the sample must be volatilized and enters the excitation zone as a vapour, the composition of which reflects that of the solid. This task has been traditionally performed by arc and spark spectroscopy which, especially in the case of powder analysis, may present a series of drawbacks in controlling atomization, reproducibility or detection power. Though a number of remarkable improvements both in instrumentation and procedures have been recently introduced, the need for alternative methods in emission spectroscopy is still keenly felt. From this standpoint, low-pressure sources, essentially the glow discharge and the hollow cathode, show remarkable capabilities, which in the case of the former have been already largely exploited when Grimm [1] first launched a new and expedient version of this excitation source.

The hollow cathode, albeit known in its basic configuration for some decades [2, 3], has not gained an equivalent popularity. This is partly in contrast with the fact that its analytical potential for the determination of minor and trace elements in organic materials would appear even superior to that of the Grimm’s emission source.

A synopsis of the above techniques is set out in Table 1.

The latest progress made in this field as a part of the Italo-Hungarian programmes of scientific cooperation will be surveyed hereafter.

### Analytical problem and instrumentation

Without going into technicalities (refer to paper 4 for details), it suffices to say that low-pressure discharges operate basically by producing a pseudo-gaseous phase from the sample the surface of which is bombarded by noble gas atoms and ions formed by the electric field applied to the electrodes inside the discharge tube. Whereas in the case of the glow discharge the flat cathode configuration involves a continuous removal of sample material from the discharge zone, the hollow cathode has the definite advantage of a much longer residence time of the sample atoms within the plasma. Moreover, the oscillating movement of electrons inside the cathode further increases the number of collisions useful for the excitation process.

**Table 1. — Techniques available in emission spectroscopy for the analysis of minor and trace elements in solid samples**

<table>
<thead>
<tr>
<th>Excitation source</th>
<th>Detection power (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Arc (direct current, alternating current, interrupted, high frequency)</td>
<td>$10^3 - 10^5$</td>
</tr>
<tr>
<td>Spark (high, medium or mains voltage, with or without control of the discharge circuit)</td>
<td>$10^0 - 10^2$</td>
</tr>
<tr>
<td>Glow discharge (normal, abnormal obstructed)</td>
<td>$10^0 - 10^2$</td>
</tr>
<tr>
<td>Hollow cathode (hot, cooled, transitional)</td>
<td>$10^1 - 10^4$</td>
</tr>
<tr>
<td>X-ray</td>
<td>$10^4 - 10^4$</td>
</tr>
</tbody>
</table>

**Fig. 1. — Block sketch of the instrumentation for hollow cathode emission spectroscopy.**
A, discharge tube; B, hollow cathode; C, cathodic block; D, anodic block; E, spectrograph; F, entrance slit; G, grating; H, film; I, pumping system; J, pressure and electric current monitoring system; K, electric power unit; L, argon supply; M, compressed air supply
An overall view of the experimental setup, discharge lamp and hollow cathode employed is given in Figs 1, 2 and 3, respectively.

Table 2 summarizes the main information on the apparatus.

Analysis of solid materials by the hollow cathode can be performed either by forming cathodes directly from the samples under study if these are machineable, or by loading the cavity of supporting cathodes with the specimens. It is obvious that the first solution is viable only when the material to be discharged is electrically conductive, as in the case of the determination of composition of metal alloys. The second case is somewhat more complicated. In fact, powders resulting from the combustion of biological samples, from airborne dusts or through grinding of minerals are as a rule poor conductors of electricity and must therefore be subjected to preliminary treatment before they can be discharged.

Pouring of loose powders into the electrode hole in order to stratify them on the bottom is a fairly unreliable practice with drawbacks such as random ejection of particles out of the cathode mouth and irreproducibility of the discharge process. An improvement of this rather simple procedure consists in pressing the powder within the cathode by hand with a glass rod thus compacting it and limiting its irregular ablation.

A much better approach to the problem consists in making the sample conductive by mixing it with appropriate materials, e.g. copper, silver or graphite, similarly to what happens in the case of glow discharge. A series of experiments were therefore planned aimed at optimizing the performance of analyses of this type by means of the hollow cathode, as reported in the following section.

Stepwise refinement

In order to test the feasibility of powder analysis by hollow cathode emission source, synthetic samples containing a number of elements of interest were prepa-

Table 2. - Characteristics of spectrograph and ancillary apparatuses

<table>
<thead>
<tr>
<th>Equipment (RSV, West Germany):</th>
</tr>
</thead>
<tbody>
<tr>
<td>Vacuum spectrograph 1 m/800 (concave grating, 1 m radius, 1200 grooves/mm, blazed at 5° 52' Paschen-Runge mounting. spectral range, 120-600 nm, dispersion, 0.78 nm/mm at 300 nm, resolving power, 30,000 at 300 nm)</td>
</tr>
</tbody>
</table>

Signal detection and evaluation:

emulsion, Kodak SA-1 films: developer, Kodak D-19 (4 min at 20 ± 0.1 °C)

microdensitometer, MD - 100 (Jenoptik, Jena. East Germany)

Excitation source:

hollow cathode lamp with electric source unit HVG 2

red by mixing their oxides with an artificial matrix resembling a typical mineral residue of organic material combustion. The mixture was spiked with Ga$_2$O$_3$ as an internal standard, and finally copper plus graphite (4:1) were added at an amount four-fold that of the starting mixture containing the analytes and the matrix.

Table 3 sets out the elements investigated and other relevant information on the samples thus prepared.

1) Procedure A. - Initially it seemed appropriate to line the entire inner surface of a supporting cathode with the sample to be discharged after adequately pressing the powder. For this purpose, powdered samples were formed as hollow cylinders using a special type of die, as shown in Fig. 4. Cylinders height should not exceed 10 mm. Beyond this, in fact, the pressure of 4 tons cm$^{-2}$ necessary to sinter the sample particles damaged the thin-walled hollow piston of the die. Pellets as high as 7.4 mm (one half of the cathode depth) could be thus obtained, two of which for each sample were then put into a supporting copper cylinder. A

![Fig. 2 - Simplified sketch of the hollow cathode tube employed for the analysis of trace elements in powdered samples. A, cathodic block; B, anodic block; C, hollow cathode; D, anode; E, glass separator; F, quartz window](image_url)
Table 3. — Composition of the powder samples analysed by hollow cathode discharge

<table>
<thead>
<tr>
<th>Analyte (A)</th>
<th>Concentration range in the final mixture (ppm)*</th>
<th>Matrix composition</th>
<th>% (B)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag (as Ag₂O)</td>
<td>5 - 600</td>
<td>KCl</td>
<td>43.8</td>
</tr>
<tr>
<td>Al (as Al₂O₃)</td>
<td>5 - 600</td>
<td>NaCl</td>
<td>47.1</td>
</tr>
<tr>
<td>B (as H₃BO₃)</td>
<td>5 - 1000</td>
<td>CaSO₄·2H₂O</td>
<td>5.3</td>
</tr>
<tr>
<td>Cr (as Cr₂O₃)</td>
<td>5 - 600</td>
<td>MgO</td>
<td>2.05</td>
</tr>
<tr>
<td>Mn (as MnO₂)</td>
<td>5 - 600</td>
<td>Fe₂O₃</td>
<td>1.75</td>
</tr>
<tr>
<td>Ni (as NiO)</td>
<td>5 - 600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pb (as PbO)</td>
<td>5 - 1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sn (as SnO₂)</td>
<td>5 - 1000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti (as TiO₂)</td>
<td>5 - 600</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Zn (as ZnO)</td>
<td>5 - 2000</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* The final mixtures contain 1 part A + 1 part B + 6 parts Cu powder + 2 parts graphite powder.

Conventional 8.0 mm die was subsequently employed for preparing flat pellets to be placed at the lower end of the hollow cylinder thus forming a hollow cathode whose inner surface was entirely coated with the sample. The flat pellets were embodied in disks of copper powder in order to limit the amount of sample necessary for the analysis without compromising mechanical resistance of the pellets themselves.

On the basis of preliminary measurements it could be ascertained that the mean size of sample particles should not exceed 40 μm, this being a threshold value for optimal sputtering of material and reproducibility of discharge.

Fig. 5 illustrates the arrangement adopted in this first procedure, whereas Table 4 reports the working conditions selected for the discharge.

The set of operative parameters thus selected produced emission spectra of good intensity and appreciable reproducibility.

It was noted that under such conditions sputtering of the sample material occurred mainly on the bottom and lower half of the cathodic wall. As a consequence, the upper cylinder did not contribute to the discharge and was simply replaced by a cylinder identical except for the absence of the analytes. This permitted the amount of sample necessary for the analysis to be decreased to 650-700 mg, without affecting analyte emission intensities.

Linearity and sensitivity of the calibration plots were found to be more than satisfactory, as testified by

Fig. 4. — Cross section of the die employed for the preparation of hollow cylindrical pellets. 1, piston; 2, die main body; 3, scaling O-ring; 4, base; 5, central peg.

Fig. 5. — Cross section of the hollow cathode for the analysis of pressed powders placed on the entire inner surface. A, sample containing pellet; B, copper supporting cylinder; C, scaling O-ring; D, copper supporting plate; E, copper pellet incorporating sample.

Table 4. — Operative conditions for the hollow cathode discharge of powders (Procedure A)

| Transport gas: Argon at 230 Pa | Anode—cathode distance: 7.0 mm |
| Applied current intensity: 400 mA | Predischarge time: 30 s |
| Resulting voltage: 370 - 410 V | Exposure time: 30 and (depending on sample composition) 60 s |
the data reported in Table 5. A calibration curve example is given in Fig. 6.

Table 5. — Figures of merit for the determination of elements in powdered samples (Procedure A)

<table>
<thead>
<tr>
<th>Element and wavelength (nm)*</th>
<th>Regression equation ( \log c = \log c' + \log (I_\text{R}) )</th>
<th>Bravais–Pearson correlation coefficient ( r )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ag 338.289 (a)</td>
<td>( \log c = 1.929 + 1.251 \log (I_\text{R}) )</td>
<td>0.99</td>
</tr>
<tr>
<td>Al 396.153 (a)</td>
<td>( \log c = 2.787 + 2.307 \log (I_\text{R}) )</td>
<td>0.99</td>
</tr>
<tr>
<td>Cr 125.435 (a)</td>
<td>( \log c = 2.146 + 1.295 \log (I_\text{R}) )</td>
<td>0.99</td>
</tr>
<tr>
<td>Mn 103.075 (a)</td>
<td>( \log c = 2.221 + 2.212 \log (I_\text{R}) )</td>
<td>0.99</td>
</tr>
<tr>
<td>Ni 352.451 (a)</td>
<td>( \log c = 2.467 + 1.154 \log (I_\text{R}) )</td>
<td>0.99</td>
</tr>
<tr>
<td>Pb 283.307 (a)</td>
<td>( \log c = 3.240 + 1.190 \log (I_\text{R}) )</td>
<td>1.00</td>
</tr>
<tr>
<td>Sn 283.999 (a)</td>
<td>( \log c = 3.150 + 1.299 \log (I_\text{R}) )</td>
<td>0.99</td>
</tr>
<tr>
<td>Ti 365.350 (b)</td>
<td>( \log c = 3.367 + 1.077 \log (I_\text{R}) )</td>
<td>0.94</td>
</tr>
<tr>
<td>Zn 307.590 (a)</td>
<td>( \log c = 3.842 + 1.273 \log (I_\text{R}) )</td>
<td>0.99</td>
</tr>
</tbody>
</table>

(a) exposure time = 30 s; (b) exposure time = 60 s

* Boron could not be determined owing to an irregular contribution from the insulating disks of pyrex around the cathode mouth to the overall emission of this element.

2) Procedure B. — The experimental evidence gained in the first part of the investigation strongly supported the hypothesis that the method could be further developed and simplified. With appropriate noble gas pressure and current intensity values, in fact, discharge concentrated mainly on the bottom surface, with a certain contribution of the lower half of the composite cathode. By carefully selecting the most suitable values for each parameters, the ratio of attacks on these two zones changed significantly giving a more pronounced sputtering of the pellet closing the cylinder. It could be therefore inferred that the emission intensities of the analytes would not be excessively altered should they be removed also from the second cylindrical pellet. Preliminary results confirmed the validity of this assumption, even though a certain degree of attack could be still observed on the cathode lower wall. In order to further decrease this it was decided to introduce some essential modifications in the cathode (illustrated in Fig. 7), consisting mainly in the removal of the two cylindrical pellets and replacement of the copper sup-

![Fig. 7](image-url) - Cross section of the hollow cathode for the analysis of powders according to procedure B. A, sample containing pellet; B, graphite supporting cylinder; C, sealing O-ring; D, copper supporting plate

![Fig. 6](image-url) - Calibration plot of Pb in powders. o, log I, 30 s; □, log I, 60 s; ●, log I/IR, 30 s; ▲, log I/IR, 60 s (procedure A)

porting cathode with graphite. It is well known, in fact, that graphite has a sputtering yield much lower than that of copper. This new version proved to be very expedient, since the degree of attack on the cathode bottom was further increased. Nonetheless, some difficulties were encountered in that discharge was not completely stable and a certain amount of graphite deposit was found on the rim of the pellet. This phenomenon was thought to be partly caused by the polarization of the insulating particles of analyte oxides contained in the specimen (see Drobysh and Turkin [5]). According to these authors, operation of the discharge under pulse conditions instead of the d.c. mode was very beneficial, as stability was restored and sputtering occurred only on the sample, whereas the graphite cathode wall was progressively covered by the redeposition of the cathodic material.

In terms of ease of operation this second procedure resulted particularly convenient as it required the preparation of flat pellets only, while the obtainment of cylinders of high purity graphite posed no problems. On
the other hand, no appreciable variations were observed in any of the parameters characterizing the analytical process. In fact, reproducibility remained unaltered and linearity of the calibration plots was still very satisfactory. The only drawback was that emission intensity decreased appreciably due to the fact that the average power available for discharge was much less per unit time with pulse operation than without. As a consequence, detection power worsened, this being partly caused also by the reduced sample surface for discharge in comparison with that of the first procedure. This difficulty could be easily circumvented owing to the very favourable line-to-background intensity ratio which permitted exposure time to be prolonged considerably.

Tables 6 and 7 summarize the experimental conditions adopted in this second instance and more relevant information on the results.

Fig. 8 illustrates as an example the behavior of one of the elements investigated.

According to previous investigations [6], another way of increasing emission intensity and simultaneously lowering background emission is to superpose a microwave field at 2540 MHz to the hollow cathode discharge. Also in this case results were positive since an increase of at least one order of magnitude for the detection limits could be obtained. It was decided therefore to operate constantly with the microwave superposition when applying pulse to hollow cathode discharge.

3) Procedure C. — A logical development of the method in 2 was to place the pellet directly within a graphite hollow cathode, as shown in Fig. 9. As a rule, results obtained under identical experimental conditions with procedures B and C practically coincided, thus confirming the validity of this further simplification. In some cases, however, a not quite perfect contact between the cathode bottom and the pellet caused local increases in temperature, with deviations from the optimal emission performance and even cracks in the pellet itself. From this viewpoint therefore, procedure B appears in practice to be more reliable, combining ease of performance with stability and reproducibility of the atomization and emission processes.

![Figure 8](image_url)

**Fig. 8** — Calibration plot of Cr in powders. ○, log $l/|l_R$, 10 min; ●, log $l/|l_R$, 10 min (procedure B)

![Figure 9](image_url)

**Fig. 9** — Cross section of the hollow cathode for the analysis of powders according to procedure C. A, sample containing pellet; B, graphite hollow cathode
Some further comments

The method described, and its variations, seems to be particularly well suited for the analysis of ashed organic materials assayed for their content in trace and minor elements.

It should be stressed that the hollow cathode as an emission source can serve as well for the analysis of liquid samples obtained from the wet destruction of biological samples. The normal procedure under such circumstances is to fill hollow cathodes of suitable material with the solutions to be analyzed, as depicted in Fig. 10 (100 - 400 μl are generally sufficient), and dried and calcined, if necessary, directly therein. The solid residues strongly adhere to the cathode inner surface and can be thus discharged without difficulty. The similarity of this type of analysis with that outlined above is self-evident in that a solid sample has been, in a way or in the order, placed into a supporting hollow cathode. In the case of solution residues an important difference lies in the absence of a conducting material. The considerably reduced thickness of the residue layer and the good electrical properties of the supporting cathode, however, make this requirement much less mandatory than for solid powders.

Application of the methods to real samples, e.g. determination of Al, As, Ga and Zn in brain, liver and kidney of rats, as well as of Ga in tumoural tissues [7, 8], was found to be very encouraging in that results compared very well with those obtained by atomic absorption spectrometry or arc emission spectrography.

A look into future

In spite of its limited popularity the hollow cathode emission source proves valuable for the determination of trace and minor elements in complex matrices such as those encountered in biological systems and environmental compartments. Its analytical potential as well as its operational flexibility allow samples mineralized either by dry-combustion or wet-ashing procedures to be equally well assayed, the choice being thus dictated only by its suitability to the particular determination under study.

When analyzing elements at very low concentration levels difficulty may arise from traces of these in the copper and graphite powders used for the preparation of pellets. The blank contribution may in fact be comparable with the analyte amounts present in the samples. Great care should therefore be taken in selecting adequate components.

Some advantages possessed by the hollow cathode for this type of analyses are particularly relevant, i.e.: a) possibility of simultaneous determination of numerous elements with a unique set of working conditions; b) wide dynamic range encompassing more orders of magnitude (not less than 2 or 3); c) low or even negligible matrix effects.

It is reasonable to forecast that this emission source will be more and more frequently employed when evaluating and monitoring the content of toxicologically and environmentally relevant elements in a variety of matrices [9].

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REFERENCES


