

Analytical Capabilities of a Microwave-coupled Hollow-cathode Discharge*

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The atomic spectrometric potential of using a hollow-cathode discharge (HCD) combined with a microwave (MW) field at 2450 MHz, particularly with regard to the determination of trace elements in solid conducting samples, pelletised materials and solution dry residues, is evaluated. Overall, improved operational stability, enhanced absolute emission intensity of spectral lines and decreased background levels afford better detection limits of at least one order of magnitude in all instances. In particular, the various aspects connected with the analysis of solutions are discussed in the light of further possible applications.

Keywords: *Microwave-coupled hollow-cathode discharge; solid sample; solution*

Over the years, the availability of low-pressure discharges has been of benefit to both the theoretical and applicative aspects of atomic spectrometry.¹⁻³ However, the potential of such sources is still under-exploited, especially if one considers their flexibility in coping with a variety of analytical and technological challenges. The hollow-cathode discharge (HCD), in particular, has been of great value in several fields of research not to mention the fact that atomic absorption spectrometry owes much of its growth and wide acceptance to the existence of this device with its ability to emit stable and sharp spectral lines (see, for example, references 4-6). Isotope ratios are also amenable to investigations with HCDs, due to their unique capabilities, and these have been well documented.⁷⁻¹⁰

A number of reviews have appeared giving accounts of the vast number of studies carried out so far on HCDs.^{3,11,12} A comprehensive picture has emerged not only of the current state of the art but also indicating future trends which may capitalise on HCDs. Such prospects have already been outlined and discussed from the point of view of what can actually be offered to the user to meet the needs of modern analytical chemistry.^{13,14}

Certainly one major drawback plaguing the HCD source in atomic spectrometry is its inadequacy in the conventional operation mode to detect and quantify elements in the low ng g⁻¹ range. One possible way of overcoming this is to power the discharge with an external form of energy, which would not affect the distinct atomisation and excitation processes of the HCD. Within this framework, superposition of a microwave (MW) field on to the HCD generated plasma has, over the last few years, provided sufficient satisfactory experimental evidence to deem the coupled discharge a promising approach deserving further investigation.¹⁵⁻¹⁸ Of the improvements associated with such a superposition, mention should be made of the noticeable increase in the intensity to background ratio and the relatively higher stability of the discharge accompanied by a slight, yet unequivocal, improvement in line sharpness. While reconsidering in general the results obtained to date in the light of present interpretations, this paper will also focus on data now available from investigations of the mechanism responsible for the performance of this combined discharge.

Instrumental Aspects

The numerous versions of the MW-HCD devised so far have led to the model shown in Fig. 1 which is probably the most

effective compromise of the contrasting requirements. The intense heat generated by the MW irradiation must be dissipated quickly and efficiently in order to avoid significant thermal effects on the inherent HCD phenomena and damage to the lamp body. For this purpose the entire tube, including the resonant cavity, is water cooled, thereby avoiding excessive over heating. However, the MW superposition *versus* volatilisation of the cathode material must still be taken into consideration, as indicated in previous studies.^{19,20} This phenomenon is qualitatively related, although in a complex manner, to the temperature of the phase transition for the material being tested. It can be assumed therefore that with relatively low melting-point metals the pseudo-vapour density in the plasma is higher with a coupled discharge than with a normal HCD. In such instances, emission intensity is thus augmented not only because of higher energy characterising the MW-HCD combination, but also because of the higher number of sample atoms entering the discharge. An example of the differences that can occur in the surface morphology under conditions for both discharges is given for Al in Fig. 2.

At present, a complete theoretical interpretation of the mechanism of the coupled discharge has not been made; this is not surprising as even the conventional HCD still presents some aspects which are not fully understood. In general, it can be stated that enhancement of the plasma ionisation due to the MW field provides a more highly energised environment for the particles entering the negative glow. This results in increased populations of both fast and thermalised electrons, the role of which is of fundamental importance in the excitation process. When Ar is used as the carrier gas it can

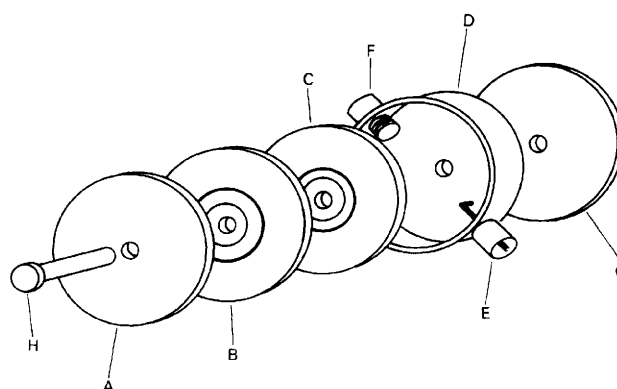


Fig. 1. Simplified exploded view of the MW-HCD lamp. A, Cathodic block; B, PTFE insulating plate; C, brass plate; D, resonant cavity; E, coupling loop; F, tuning stub; G, anodic block; and H, hollow cathode

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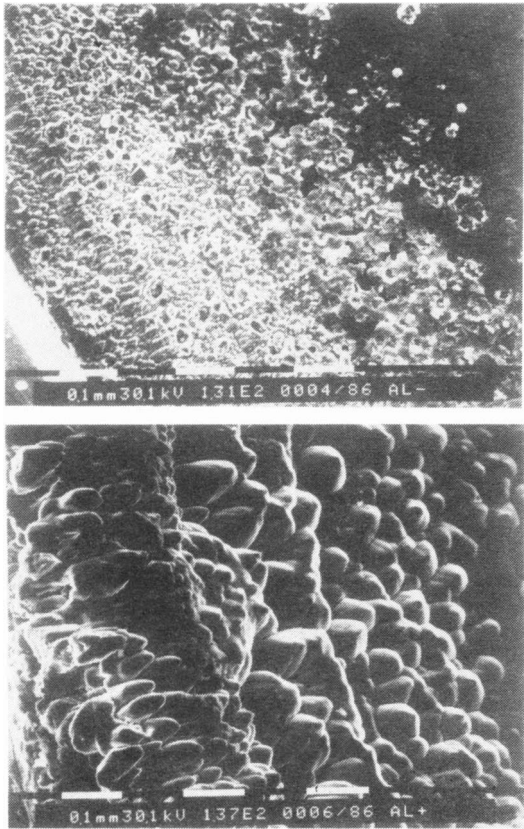


Fig. 2. Sputtered surface of Al at a magnification of ca. 100 ×. (a) with HCD and (b) with MW-HCD

also be assumed that a higher density of gaseous metastable atoms are generated, which is in agreement with recent findings.²¹

In order to minimise the loss of applied MW power the cavity quality factor (Q) must be as high as possible.²² This is in fact a parameter that is inversely related to the skin depth, which is minimal for silver and copper and slightly increases for gold and aluminium at a given MW frequency. For a number of reasons these materials show practical drawbacks, which make brass a preferable material for machining the cavity from, although its Q value is not too high (0.48). Brass was therefore chosen for the construction of the resonator while the anodic and cathodic blocks of the lamp were made from a Cu - Be alloy. The Q factor can be further enhanced by plating the cavity with silver although problems may arise during lamp operation if adherence of the metal layer is not perfect. The tuning stub greatly facilitates alignment of the lamp optical axis with the most intense zone of the microwave-induced plasma (MIP). When both discharge modes are operated simultaneously there is a visible increase in the over-all luminosity characteristic of each. Moreover, the plasma glowing inside this electrode cavity is seen to protrude from the cathode mouth slightly more than with conventional HCD sources, while at the same time it coalesces with the MW luminescent column along the tube axis. In practice the two emission processes reinforce each other and apparently merge into one.

One of the main advantages offered by the combined device is that the two processes of atomisation and excitation can be, at least in part, controlled separately. Although there is room for considerable improvement, this type of boosted tube further extends the range of applications of conventional HCDs. Table 1 lists essential information on the MW-HCD lamp and ancillary instrumentation. Both Ar and He can be

Table 1. Apparatus employed

Generation of spectra —	
Discharge lamp	Demountable water-cooled hollow-cathode tube equipped with a MW resonant cavity of the Beenakker type
Generators	Current intensity: HVG 2 stabilised unit with output up to 500 mA (RSV Präzisionsmessgeräte, Hechendorf, FRG) MW power: Radarmed 12 S 230 operating at 2450 MHz with output up to 220 W
Meters	Thermotron TM 11/2 with reading range, 0.1–1000 Pa (Leybold-Heraeus, FRG) Voltage: digital multimeter 3476 A with range 1–1000 V (Hewlett-Packard, Palo Alto, CA, USA)
Carrier gas	Ar, 100–1000 Pa He, 100–1000 Pa
Evacuation and gas circulation	Double-stage oil pump with a 16 l min ⁻¹ pumping speed (Leybold-Heraeus, Hanau, FRG)
Recording of spectra—	
Spectrographs	1 m/800, Paschen-Runge mounting, equipped with two concave gratings of 1200 and 2400 grooves mm ⁻¹ , spectral range 120–500 nm, entrance slit width 30 µm (RSV Präzisionsmessgeräte, Hechendorf, FRG) PGS 2, Ebert mounting, equipped with two plane gratings of 600 and 1200 grooves mm ⁻¹ , spectral range 200–900 nm, entrance slit width 40 µm (Jenoptik, Jena, GDR)
Detection system	Photographic emulsion Kodak Spectrum Analysis No. 1, supported either on plates or films Developer Kodak D-19 at 20 °C for 4 min Microdensitometer MD-100 (Jenoptik, Jena, GDR)

used as the noble gas for the discharge depending on the circumstances, although from a general point of view, the first appears to be better in terms of relative increase in spectral intensity. It should also be emphasised that the spectra were almost always dispersed using the described 1 m/800 spectrograph (RSV, Hechendorf, FRG) as it is possible with this instrument to record the entire spectral range from 200 to 450 nm (120–450 nm when the spectrographic chamber is under vacuum) on one single 1-m long strip of film. Finally, in order to speed up the optimisation of the working conditions, in some instances an H20 Vis monochromator (ISA Instruments, France) incorporating a direct reading system was used.

Examples of Applications

The very nature of the HCD makes it suitable, at least in principle, for the determination of virtually all elements in a variety of matrices. Samples should preferably be in the solid state and electrically conductive to enable easier transfer of atoms or clusters of atoms into the excitation zone to effect the ionic bombardment. Refractory materials cannot be subjected directly to the HCD as they give rise to polarisation phenomena while the direct spraying of solutions into the HCD plasma is in turn hindered by the ensuing instability of the discharge process caused by the quenching effect of water vapour. All of these constraints can be easily overcome by conventional methods.^{23,24} This is more relevant when using a MW-HCD where, as although trace element detection is easier, the same problems of specimen preparation are encountered.

Metals and Alloys

A number of investigations have been carried out to ascertain the capabilities of the MW-HCD technique in the quantification of minor and trace components in solid materials. A preliminary survey of the behaviour of several pure metals when discharged in the composite lamp provided consistent results insofar as there was a general increase in emission intensity, although the behaviours were very different from element to element and from line to line.¹⁵ This pattern is qualitatively summarised in Table 2. As such materials can be used to machine massive cathodes to serve as support electrodes for the discharging samples contained in their cavities, it is useful to know in advance whether a line emitted by the hosting electrode is proportionally less enhanced than one from the analyte at approximately the same wavelength. This could actually help in avoiding potential spectral interferences if the support element is carefully selected on the basis of the chosen analytical line (and *vice versa*). Moreover, more specific studies have demonstrated the validity of the over-all approach. Chromium and Ni in low-alloy steel, for instance, can be determined with an improvement in detection power of one order of magnitude.¹⁵ Similar results have been obtained in quantifying some minor elements (Cu, Mg and Mn) in a set of Al alloys.¹⁶ In this instance, the concentrations to be measured ranged from 0.012 to 5.85% and thus did not pose difficulties even with the conventional HCD. It is however, reasonable to infer that the positive difference in intensity in favour of the MW-HCD will be retained at much lower levels. A definite advantage is the actual improvement in the stability of the discharge and a decrease in the self-absorption, which affects some of the fundamental Cu lines in the normal HCD. Another important example is the determination of P in steel and copper specimens. As a consequence of the severe spectral interference caused by the Ar carrier gas on the P lines at 178.29, 178.77, 185.89 and 185.94 nm, it is essential that He is used instead. Even using this rare gas, spectra of great complexity are generated with steel samples and therefore reliable determinations cannot be performed. With the copper matrix, on the contrary, concentrations of P as low

as 0.02% can be easily measured. However, this analysis proves to be rather laborious and is hindered by the poor sputtering ability of He, although, it should be borne in mind that the conventional discharge is entirely inadequate.

Non-conductive Samples

Substances such as minerals, ores and biological materials after combustion cannot be analysed in a straightforward manner by the HCD, mainly because of their poor electrical conductivity. The simple loading of loose powders into supporting cathodes cannot be considered satisfactory, given the unreliable behaviour of the particles within the cathode and of the volatilisation process. The analytical capability improves considerably when the samples are ground to an average particle size of a few tens of a micrometre, mixed with a convenient amount of a conducting substance (*e.g.*, copper, silver, gold or graphite) of the same granular size and compacted into pellets of a suitable shape under a pressure of several tons cm⁻².¹⁸ Under such conditions the ablation of the sample surface is regular and reproducible, the only disadvantage being that the analytes are now diluted by the mass of the binder in a ratio of 1:3 or more. This drawback almost disappears with the MW-HCD as the increase in emission more than compensates for this detrimental effect. A key role in this procedure is obviously played by the purity of the dispersing material.

There are also similar problems with solutions, in that the solvent, which affects the analysis, must first be removed to obtain the mineral dry residue. However, the main difference between solutions and solids analysis is that only a very thin film of the salts is generally left behind which cannot be treated in the same way as discussed above. Moreover, it is clearly advisable that the entire process be carried out with minimum sample manipulation in order to minimise the risk of contamination and time necessary to perform the determinations. Therefore, the solution is placed into the bore of a support cathode (which should be as chemically inert as possible) and desiccated directly in this before subjecting it to the discharge. A deposit of dried salts is thus obtained at the bottom of the cathode, which provides the possibility of repeating the procedure whenever concentrations of the elements under investigation fall below the detection power of the HCD system.

When considering the great variety of liquid samples that can be presented for analysis, it is apparent how the combined discharge can significantly extend the scope of this spectroscopic method, particularly for quantification of trace elements in biological fluids. The limited amount of information available in this area is nonetheless encouraging. Elements such as Al, As, Cu, P, Pb and Zn have been determined with better detection limits than those achievable with the normal HCD.^{15,17} On the basis of these preliminary findings it was decided to investigate further the behaviour of these types of samples. Thus, a number of solutions containing four cations at various concentrations were studied with both excitation devices using the working conditions detailed in Table 3. In accordance with the normal procedure, several tenths of a millilitre of sample are dispensed into the cathode cavity and

Table 2. Influence of the MW field on the HCD emission of some metals in Ar

Element	Spectral line/nm	Intensity variation*	Conditions
Al	257.51	B	HCD: $I = 300$ mA,
	1265.25	B	$V = 310$ V, $p = 426$
	1266.04	B	Pa. MW-HCD: $I =$
	1394.40	C	300 mA, $V = 300$ V,
Cu			$p = 426$ Pa, MW =
			200 W†
	1224.70	D	HCD: $I = 300$ mA,
	1299.74	D	$V = 400$ V, $p = 426$
Mo			Pa. MW-HCD: $I =$
			300 mA, $V = 380$ V,
			$p = 426$ Pa, MW =
			200 W†
Zn			HCD: $I = 100$ mA,
			$V = 290$ V, $p = 426$
			Pa. MW-HCD: $I =$
			100 mA, $V = 280$ V,

* Extent of increase: A, not appreciable; B, below 10%; C, between 10 and 50%; and D, above 50%.
† Nominal power of applied MW field.

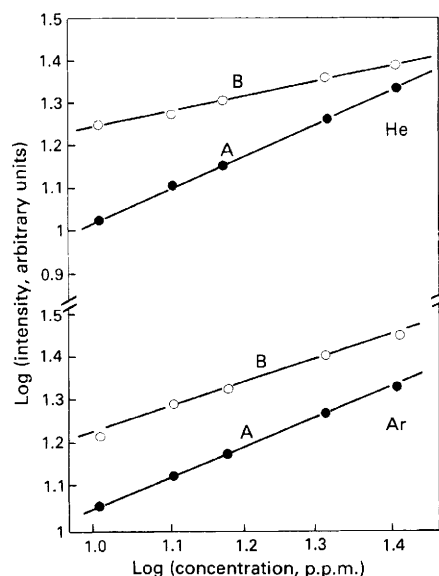
Table 3. Conditions for analysis of multi-element solutions

Element wavelength/nm	Cr 403.91, Mn 406.17, Ni II 247.31 and Pb I 405.78
Concentration mg/l ⁻¹	0.1, 0.5, 1.0, 2.5, 5.0, 10.0, 20.0, 25.0 and 30.0
Carrier gas pressure/Pa	Ar 100; He 600
Current intensity/mA	Ar 200; He 300
Resulting voltage/V	Ar 350 – 550; He 200 – 440
Exposure time/s	60
MW power/W	200 (nominal value)

Table 4. Calibration equations for the determination of elements in solution residues

Element and line/nm	Carrier gas			
	Ar		He	
	HCD*	MW-HCD*	HCD*	MW-HCD*
Cr 403.91	$\text{Log}C = 2.8 \log I - 3.1$ ($r = 0.99$)	$\text{Log}C = 2.2 \log I - 2.3$ ($r = 0.99$)	$\text{Log}C = 3.7 \log I - 4.4$ ($r = 0.96$)	$\text{Log}C = 5.2 \log I - 8.7$ ($r = 0.98$)
Mn 406.17	$\text{Log}C = 2.1 \log I - 2.3$ ($r = 0.99$)	$\text{Log}C = 3.3 \log I - 4.4$ ($r = 0.99$)	$\text{Log}C = 1.7 \log I - 1.8$ ($r = 0.97$)	$\text{Log}C = 6.6 \log I - 9.9$ ($r = 0.99$)
Ni II 247.31	$\text{Log}C = 1.6 \log I - 0.7$ ($r = 0.99$)	$\text{Log}C = 1.5 \log I - 0.9$ ($r = 0.99$)	$\text{Log}C = 1.4 \log I - 0.4$ ($r = 1.00$)	$\text{Log}C = 2.6 \log I - 2.2$ ($r = 1.00$)
Pb I 405.78	$\text{Log}C = 0.9 \log I - 0.1$ ($r = 0.99$)	$\text{Log}C = 3.0 \log I - 3.5$ ($r = 0.99$)	$\text{Log}C = 4.3 \log I - 4.5$ ($r = 0.98$)	$\text{Log}C = 4.2 \log I - 5.1$ ($r = 0.99$)

* C = concentration (mg l^{-1}); I = emission intensity (arbitrary units); r = Bravais - Pearson correlation coefficient.

**Fig. 3.** Calibration graphs for Ni II 247.31 nm in Ar and He; A, with HCD and B, with MW-HCD

carefully evaporated under IR irradiation so that a uniform, strongly adhering salt film can precipitate. In this instance, 400 μl of the multi-elemental aqueous solutions are loaded into stainless-steel electrodes, which have the advantage of being resistant to the corrosive action of aggressive liquids. Independent of the solution concentrations, all samples were characterised by an initial short period (5–10 s) of discharge instability followed by the establishment of relatively constant voltages, which tended, however, to decrease with time as the salt film was progressively fired out. To complete the sputtering of samples within the cathode discharge a duration of 1 min was deemed more than adequate, thus providing a sufficiently long integration of the analytical signals.

After processing the photographic emulsion, measurements of the blackening of spectral lines of interest and of the background were carried out and the corresponding values transformed into I -values according to usual densitometric procedures, this in turn permitting emission intensity values to be quickly deduced.²⁵ Calibration equations for the concentration ranges spanned were calculated as shown in Table 4. These relationships and the corresponding plots clearly show that not only is good linearity attainable but also the inherently higher detection power that characterises the MW-HCD source. An example of such a graph is given in Fig. 3. Moreover, it should be taken into account that the background intensity in the spectral region considered is very low even with the simple HCD excitation mode and that it undergoes further reduction with the MW-HCD source by a

Table 5. Detection limits of the MW-HCD source in comparison with other spectroscopic methods

Element	Detection limit/ μg			
	HCD*	MW-HCD†	ETA-AAS‡	ICP-AES‡
Cd	80 000	6000	0.3	2 000
Cu	200 000	13 000	2	3 000
Pb	80 000	9000	2	30 000
Se	80 000	4000	50	60 000
Zn	160 000	10 000	0.5	2 000

* See reference 18.

† See reference 26.

‡ See reference 27.

factor of 1:3 to 1:4. When this fact is combined with the increase in absolute emission intensity brought about by the MW superposition, the new detection limits for the four elements in solution are improved by at least one order of magnitude. In this connection it is also useful that the increase in emission for the spectral lines of noble gas are either comparatively lower than in the instance of analytes (for Ar) or practically negligible (for He). The determinations can thus be performed in the presence of a relatively less interfering carrier gas spectrum.

An appraisal of the detection power inherent to the combined discharge as compared with that of the other two more popular techniques, namely inductively coupled plasma atomic emission spectrometry (ICP-AES) and electrothermal atomisation atomic absorption spectrometry (ETA-AAS), is reported in Table 5 for some representative elements.^{26,27} Although the detection limits of the MW-HCD source are clearly less favourable, it should be borne in mind that this technique is still in its infancy and that further improvements in its detection ability can reasonably be expected.

As an example of the practical application of this device, human serum samples of subjects undergoing chemotherapy with platinum-based anti-tumour drugs were analysed for their platinum content. After a careful preliminary study aimed at selecting the most suitable cathode material for hosting the liquid specimens, preference was given to graphite. This material, unlike aluminium, copper and steel, did not give rise to a spectrum that severely interfered with the lines emitted by Pt. The procedure adopted consists of degassing the graphite cathodes in a muffle furnace at 400 °C for 8 h, cooling and dispensing 100- μl aliquots of the serum samples (diluted 1 + 1 with doubly distilled water) into the cathode bore and then removal of the solvent by IR radiation. In all instances the treatment was repeated four times to guarantee that a sufficient amount of analyte would be deposited on the cathode bottom without diffusing irreproducibly into the graphite mass. The results obtained are significant in that the MW-HCD source considerably improved the platinum signal in the low $\mu\text{g l}^{-1}$ range, which is the region of interest for the

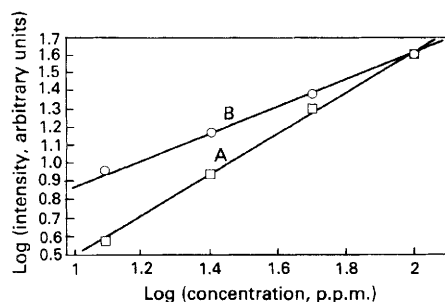


Fig. 4. Calibration graph for Pt in serum samples. Spectral line, Pt I 330.19 nm. A, with HCD and B, with MW-HCD

administered element.³⁰ The calibration equations calculated for the two excitation modes are $\log C = 1.6 \log I - 0.68$ (HCD, $r = 0.999$) and $\log C = 1.5 \log I - 0.91$ (MW-HCD, $r = 0.999$), the respective plots being illustrated in Fig. 4. For unknown samples good agreement was found with the data provided by ICP-AES, in no instance did the relative difference in concentration for the two methods exceed 2.3% for a platinum content in the $1\text{--}5 \mu\text{g l}^{-1}$ range.

Conclusion

The additional experimental evidence provided by this work strengthens the assumption that the MW-HCD atomisation and excitation device is potentially suitable for development into an alternative analytical technique. While none of the fundamental aspects of the HCD processes are adversely affected, the over-all performance of the source guarantees a more suitable analytical performance for present needs. This can be achieved using relatively low cost instrumental facilities which do not require excessively complicated operation. Although further research is required to explore the applicability of MW-HCD spectrometry fully, and to understand important aspects of the phenomena involved better, there is no doubt whatsoever that it can be integrated with more popular methods. To gain acceptance and to be developed further, MW-HCD and allied approaches^{25,26} must now emerge from specialised laboratories and be tested for their practical value. Whether this will happen in the near future is hard to say even though developments in this field are promising.

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