

The Use of a High Temperature Hollow-cathode Lamp for the Spectrographic Analysis of Steels, High Temperature Alloys and Related Materials for Trace Elements

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A study has been made of factors affecting the operation of high temperature hollow-cathode lamp discharges for the emission-spectrographic determination of trace elements in steels, high temperature alloys and related materials. The factors studied include electrode geometry, carrier-gas pressure and exposure times. The effect of these parameters on element sensitivity and the precision of analysis is discussed.

The analysis of dissimilar alloy types has been shown to present problems associated with inter-element effects, and the magnitude of these effects is illustrated. A simple method for overcoming inter-element effects is described, involving the addition of silicon as a buffer to both samples and standards. Results by this method for the analysis of a wide variety of materials from calibration graphs based on a single set of synthetic powder standards are presented. It is possible by this technique to obtain quantitative trace-analysis results without the necessity of providing chemically analysed standards.

THE hollow-cathode discharge source originally described by Paschen^{1,2,3} has since found wide acceptance for applications normally considered difficult with conventional spectrographic sources.

The technique has successfully been applied to the determination of sulphur and the halogens,^{4,5,6,7,8} and for the extensive trace analysis of refractory oxides and metals.^{9,10,11,12,13} The early work of Rosen¹⁴ and subsequent studies by Webb and Webb^{15,16} have shown the potentialities of the method for the determination of gases in metals. More fundamental studies, correlating ionisation effects and physical properties of the discharge with, *inter alia*, carrier-gas pressure and cathode geometry have been published by Mitchell¹⁷ and van Voorhis and Shenstone.¹⁸ The latter investigators made no attempt to relate the variables studied to factors such as element sensitivity or analytical precision.

Few reports have appeared in the literature concerning the use of this type of source for the analysis of non-refractory metals such as steels and nickel-base alloys. However, a paper by Mitchell and Harris¹⁹ referred to the analysis of copper and nickel for a limited number of elements.

The manufacture of nickel-base alloys and steels for high temperature applications requires close control of certain impurity elements. Conventional d.c. arc spectroscopy is often suitable, but with the many different alloy types produced the effective standardisation for such procedures is generally inconvenient and often impracticable. The intention in the present studies of the hollow-cathode source was to provide a method for the simultaneous determination of a large number of trace elements in a wide variety of alloy types and their associated raw materials.

APPARATUS—

The equipment may conveniently be considered in three parts: the hollow-cathode lamp; the inert gas supply and circulation unit; and the electrical source unit.

HOLLOW-CATHODE LAMP—

The lamp is basically a water-cooled chamber machined, in this instance, from stainless steel (Fig. 1). The inner cylindrical chamber is about 4 inches long, with a diameter of 2½ inches, and can be filled with an inert atmosphere through the gas-circulation tubes,

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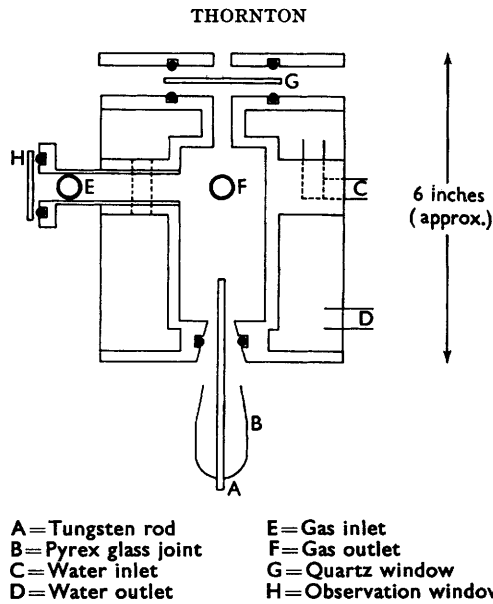


Fig. 1. Hollow-cathode lamp

E and F. A front port allows radiation to pass from the discharge region through a quartz window, G, which is mounted between O-ring seals. The discharge can be observed visually through the glass window, H, attached to the viewing port.

Graphite hollow-cathode electrodes are mounted by push-fit on a 2 mm diameter tungsten rod, A, which is sealed into the end of a B24 type Pyrex ground-glass joint, B. This joint fits into a corresponding taper machined in the rear of the lamp and is protected by an O-ring seal. The assembly is water-cooled through tubes C and D.

Operation of the lamp in the vertical position is made possible by the use of a front-surfaced mirror positioned above the quartz window, G, or, as in these experiments, in a horizontal position, by pointing the discharge port directly at the slit of the spectrograph. The separation between cathode and anode (lamp body) is not critical for this design of lamp.

The basic lamp design is similar to that used by Webb and Webb for their studies of gas determination in metals.^{15,16}

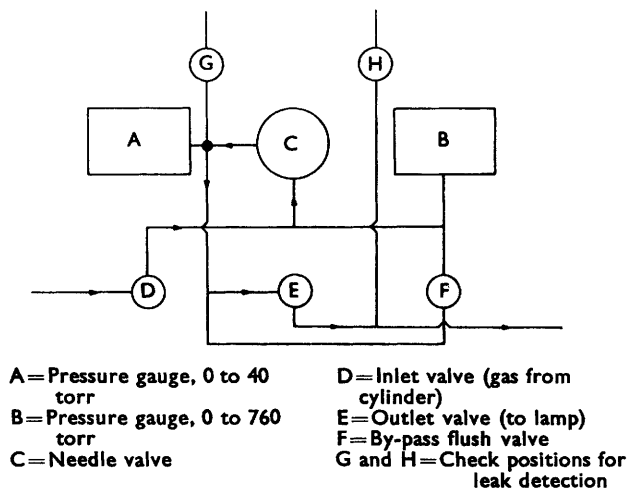


Fig. 2. Gas-circulation system

INERT GAS SUPPLY AND CIRCULATION SYSTEM—

As this type of discharge is severely affected by the presence of atmospheric pollutants (oxygen and water vapour in particular), it is essential that all joints should be vacuum-tight. In some instances, purification of the inert carrier gas may be needed, but this has not been found necessary with the supply of mineral helium used in this laboratory.

A schematic representation of the gas-circulation system is shown in Fig. 2. The helium, at 2 to 3 lb inch⁻² above atmospheric pressure, is restricted by a fine-control needle valve, C, and the pressure on the output side of this valve is monitored with a capsule-type gauge, A. Gas is pumped through the hollow-cathode lamp by a rotary pump, with a displacement of about 50 l minute⁻¹, and continuously exhausted to atmosphere. The working pressure is adjusted by means of valve C.

To facilitate rapid sample changing, a by-pass valve, F, is provided which, when opened, will bring the lamp to slightly above atmospheric pressure. This eliminates the necessity for frequent air-releasing of the rotary pump and enables the operator rapidly to flush the lamp with helium gas after sample changing.

ELECTRICAL SOURCE UNIT—

Samples are placed inside cylindrical electrodes and vaporised by the sputtering action of charged particles of the inert gas. Ionic collisions of the second kind between vaporised sample and charged-gas particles result in the excitation of the characteristic spectrum of the sample. Useful emission spectra have been obtained with currents above 200 mA sustained by potentials between 300 and 1200 V. The rectifying system shown in Fig. 3, which produces currents up to 1½ A at 400 to 500 V, has been found satisfactory. Lamp current is controlled by the auto-transformer supplying the main transformer.

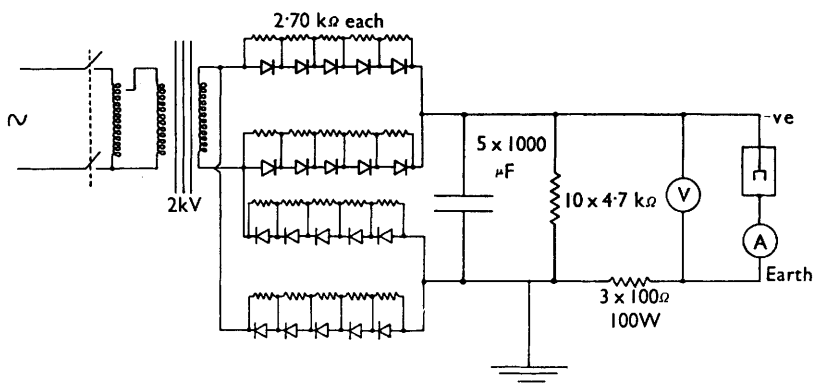


Fig. 3. Electrical source unit

OPERATING PROCEDURE—

Metallic samples are analysed in the form of turnings, millings and chippings, but powders require briquetting to avoid instability of the discharge.

Weighed amounts (10 to 100 mg) of the sample are loaded into fresh graphite hollow cathodes and inserted into the lamp. The chamber is evacuated, flushed with helium, re-evacuated, and the operating pressure adjusted by a needle valve. The discharge is initiated, and a current of about 200 mA obtained by adjustment of the auto-transformer. The spectrum is photographed, the current increased and the spectrum again photographed, the spectra being superimposed. This sequential power sweep is continued until a current has been attained that is sufficiently high to effect vaporisation of all of the elements to be determined. In practice, it is convenient to use currents up to about 1 A. This permits the analysis for a large number of elements without undue over-exposure of the matrix elements.

The spectra are dispersed by means of a Hilger and Watts Large Quartz Spectrograph and photographed on Ilford Ordinary N30 plates, which are developed in Agfa Rodinal (diluted 1 + 40 with water) for 3 minutes at 68° F and fixed with Ilford Hypam. New plate batches are calibrated by the two-step iron-arc method.

The percentage transmission values are recorded for the element lines and the internal standard line (Table I) and converted into relative logarithmic intensities by using the emulsion calibration curve. These values are plotted against logarithmic concentrations of the impurity elements. No background correction is necessary.

The stability of the discharge can be improved by prolonged out-gassing of the graphite crucible (up to 40 minutes is required for this operation), whereupon the sample can be exposed with a single, high current setting. This reduces exposure times but considerably increases total operating times. The system used by Webb and Webb^{15,16} incorporates an automatic sample changer with multiple determinations, with the same crucible. Under these conditions out-gassing is economical, but the system described here necessitates single use of the crucibles.

TABLE I
WAVELENGTHS OF LINES USED FOR QUANTITATIVE STUDIES

Element	Element line, nm	Reference line, nm
Antimony	259-806	} Helium 294-510
Arsenic	234-984	
Bismuth	289-797	
Bismuth	306-772	
Cadmium	326-106	
Calcium	317-933	
Calcium	396-847	
Gallium	294-364	
Indium	325-609	
Lead	283-307	
Silver	328-068	
Tellurium	238-576	
Thallium	276-787	
Tin	286-333	
Tin	317-502	
Zinc	255-796	

FACTORS AFFECTING SENSITIVITY—

Electrode geometry—Samples of graphite powder doped with oxides of impurity elements were pressed into pellets and exposed under constant conditions by using a variety of cathode shapes. Both the internal depths of the cathodes and the internal diameters were varied, the former from 15 to 50 mm and the latter from 4 to 8 mm. High purity graphite (Ringsdorff grade RWO) was used for the preparation of all electrodes and the wall thickness was kept constant. A total exposure time of 7 minutes was used, with a current sweep up to 1.40 A.

Fig. 4 indicates the effect of variable electrode depth on sensitivity for a selection of elements. It is seen that for each element, maximum sensitivity is obtained at a specific cavity depth and, further, that the less volatile elements exhibit maximum sensitivity with short electrodes. By increasing the length of the electrode, the spectral emission of these elements is reduced and that of the more volatile elements increased. As it is often the latter group that produces deleterious effects in high temperature alloys, this property can be used to obtain selective enhancement.

The effect of increasing the internal diameter of the cathode was more uniform. In all instances, sensitivity decreased sharply, probably as a result of a lower concentration of vapour on the viewing axis of the electrode.

By using this information in the context of the specific problems encountered in our laboratories, it was concluded that optimum conditions would be achieved with electrodes of internal length 25 mm and internal diameter 4 mm. This gives reasonably low spectral density from most of the matrix elements, *e.g.*, nickel, cobalt, chromium and iron, coupled with high sensitivity for the elements of interest, *e.g.*, lead, zinc and antimony.

Carrier-gas pressure—The effect of pressure on sensitivity has been studied for the range 5 to 30 torr. Exposures were made by superimposing current steps up to a maximum of 1.20 A.

Fig. 5 shows typical variations for line relative intensities with increasing gas pressure and, as before, it can be seen that volatile elements exhibit significantly different relationships from the less volatile elements. Unfortunately, lamp stability is not good at pressures in excess of 20 torr, this being the optimum value for good stability and sensitivity.

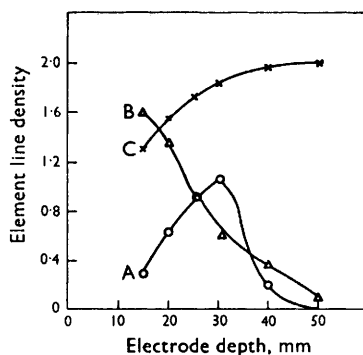


Fig. 4. Effect of electrode depth on element line density: A, antimony, 259.8 nm; B, cobalt, 340.5 nm; and C, thallium, 276.7 nm. (The more conventional relative intensity scale is replaced by line density measurements to emphasise the effect over a wide line density range)

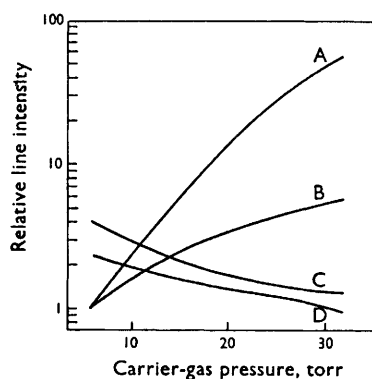


Fig. 5. Relative line intensity values for varying gas pressure: A, silver, 328.0 nm; B, bismuth, 289.8 nm; C, iron, 248.8 nm; and D, aluminium, 308.2 nm

FACTORS AFFECTING PRECISION—

Exposure time—In the previous discussion of operating procedure, it was indicated that lamp current is varied during the course of an exposure, starting at low values and increasing until a current is reached that will effect distillation of all of the elements to be determined. This is achieved by adjustment of the auto-transformer setting. In practice, this setting is varied by constant pre-determined increments, the amounts of these being governed by general discharge stability. The exposure time of each step has been varied from 30 seconds to 2 minutes and coefficients of variation calculated for a series of elements. Sensitivity was virtually unaffected, but it can be seen from the mean coefficients of variation in Table II that precision deteriorates below step exposures of 1 minute. No improvement is obtained with longer exposures.

Carrier-gas pressure—No quantitative results are available, but instability increases outside the range 10 to 20 torr, with consequent reduction in precision.

TABLE II
EFFECT OF STEP EXPOSURE TIME ON ANALYTICAL PRECISION

Step exposure time, minutes	Total exposure time, minutes	Mean coefficient of variation, per cent.
0.5	3	16.3
1	6	10.2
2	12	10.6

ELEMENT DISTILLATION—

Studies have been made of the distillation of elements from a graphite matrix by relating lamp current (and hence temperature) to element line intensity. Selective volatilisation occurs and can be used to separate the emission lines of elements to be determined from the spectra of the matrix elements. This provides an effective method of overcoming problems associated with high spectral background and line interferences often encountered with complex alloys. Thus, for instance, the tellurium line 238.576 nm is often unusable in the presence of chromium (238.576 nm) and cobalt (238.582 nm). However, with hollow-cathode analysis, it is possible to distil off the tellurium completely at a lamp current of 0.75 A (3 minutes' exposure would be sufficient for low concentrations), with no significant evaporation of either of the other two elements and consequently no interference.

TABLE III
DISTILLATION OF ELEMENTS FROM GRAPHITE IN A HOLLOW-CATHODE DISCHARGE LAMP

Lamp current, A	Elements completely distilled
0.5	Ag, Cd, Hg, Tl, Zn
0.75	Bi, In, K, Na, Pb, Sn, Te
1.0	As, Cu, Ga, Mg, Mn, Sb
1.25	Ca, Ge
≥ 1.5	Al, B, Be, Co, Cr, Fe, Ni, Si

The lamp currents at which some elements distil are shown in Table III. Distillation starts at lower currents than those indicated, the values shown being those for effective complete evaporation.

OCCURRENCE AND EXTENT OF MATRIX EFFECTS—

In the literature on hollow-cathode excitation, efforts have been concentrated on describing techniques to improve sensitivity (often by orders of as much as 10^3), or on the analysis for elements normally considered difficult to excite, *e.g.*, sulphur and the halogens. An extensive survey has shown that authors have considered either the analysis of single or closely related materials, or when diverse compounds have been analysed, standards were prepared for each type. The problem of inter-element effects has not been discussed in any detail and, indeed, little reference to this aspect can be found. It might be expected that, as distillation is closely controlled and excitation is achieved in the presence of an inert gas, such problems would be negligible or non-existent.

To check the validity of this assumption, a sample of specially melted nickel containing many of the elements of interest was analysed. The concentrations of the impurity elements were first established by spectrochemical analysis involving two techniques, namely dissolution-oxidation procedure by the well known Jaycox method²⁰ and carrier-precipitation with hydrogen sulphide.²¹

Calibration graphs were obtained for a series of such nickel standards by using the optimum hollow-cathode conditions (see Table IV). One of the samples was then analysed in the presence of additional pure elements. The selected sample was placed in a graphite hollow-cathode electrode and an equal weight of the selected element added. The analysis was carried out under the same conditions as those for the preparation of the calibration graphs. The element concentrations found by using these calibration graphs (*i.e.*, based on pure nickel) are compared with the accepted values in Table V.

Obviously, severe inter-element effects occur, particularly in the determination of the elements, gallium, tin, indium and antimony. The effect is less pronounced for some others, notably those with very low boiling-points.

TABLE IV
OPERATING CONDITIONS FOR HOLLOW-CATHODE LAMP

Carrier gas	Mineral grade helium
Gas purification	None
Gas pressure	20 torr
Internal length of graphite electrode	25 mm
Internal diameter of graphite electrode	4 mm
Anode-to-cathode distance	About 4 cm (not critical)
Exposure time (pre-burn)	Nil
Exposure time (total)	1 minute at 0.20 A 1 minute at 0.40 A 1 minute at 0.60 A 1 minute at 0.80 A 1 minute at 1.00 A
	} Superimposed
Spectrograph	Hilger Large Quartz E.742
Slit width	10 μ m
Wavelength range	235.0 to 320.0 nm and 280.0 to 495.0 nm
Source-to-slit distance	20 cm
Condensing system	F.1025 quartz lens, 2 cm from slit

ELIMINATION OF MATRIX EFFECTS—

The most severe effect is produced by silicon (see Table V). It was reasoned that an excess of this element might, when added to both samples and standards, diminish the effect of other elements. The validity of this assumption is indicated in Table VI, which shows results for the analysis of a sample of nickel by using a complex high temperature alloy for standardisation, with a 30 per cent. addition of silicon to samples and standards. The silicon used was Specpure grade metal lump (Johnson Matthey and Co. Ltd.).

TABLE V
EFFECT OF ADDED ELEMENTS ON THE ACCURACY OF HOLLOW-CATHODE DISCHARGE ANALYSIS

Added element	Element concentration found, per cent.									
	Ag	Zn	Sb	Tl	Pb	Ga	Bi	Sn	In	
Chromium	0.0043	0.021	0.026	0.0060	0.0044	0.025	0.0030	0.0031	0.0085	
Molybdenum	0.0034	0.019	0.022	0.0043	0.0040	0.023	0.0023	0.0038	0.0095	
Silicon	0.0047	0.021	0.125	0.0054	0.0038	> 0.25	0.0032	0.035	0.021	
Aluminium	0.0020	0.027	0.058	0.0054	0.0038	0.14	0.0023	0.0038	0.014	
Titanium	0.0061	0.018	0.071	0.0023	0.0044	0.11	0.0027	0.013	0.019	
Copper	0.0021	0.032	0.004	0.0051	0.0037	0.0021	0.0016	0.0005	0.0010	
Spectrochemical analysis	0.0036	0.023	0.010	0.0046	0.0040	0.0070	0.0025	0.0015	0.0050	

For comparison, the values obtained for the analysis of this nickel sample from the same high temperature alloy standards are shown without the addition of silicon. The complex alloy standards used for calibration purposes contained significant concentrations of many of the matrix elements shown in Table V, namely, chromium, molybdenum, aluminium and titanium.

TABLE VI
ELIMINATION OF MATRIX EFFECTS BY THE ADDITION OF SILICON
Analysis of unalloyed nickel by using complex high temperature alloy standards

Addition	Element concentration found, per cent.							
	Ag	Zn	Sb	Pb	Ga	Bi	Sn	
No addition*	0.0028	0.020	0.0011	0.0032	0.0006	0.0022	0.0002	
Silicon added†	0.0034	0.024	0.010	0.0038	0.0076	0.0022	0.0017	
Accepted analysis	0.0036	0.023	0.010	0.0040	0.0070	0.0025	0.0015	

* No additions made to either the nickel sample or the high temperature alloy standards.

† 30 per cent. w/w of silicon added to both sample and standards.

Results in Table VI show that the assumption that silicon would mask matrix effects caused by other elements is fully justified, and its addition provides a basis for the analysis

of a wide variety of materials. Further experiments with a larger selection of added elements have indicated that accurate results can be obtained on all matrix types except those that are highly volatile, *e.g.*, zinc, copper or aluminium base.

The amount of silicon needed for optimum results has been studied, and it was found that 30 per cent., or more, of the weight of sample is required for total elimination of matrix effects. The effect of adding extra silicon is to produce increasingly unstable discharges, with consequent decrease in precision. On the basis of these results, an addition of 10 mg of silicon is made to the weight of sample normally taken (30 mg).

STANDARDISATION—

In an attempt to eliminate the necessity for relying on chemically analysed samples for the preparation of working curves, samples of high purity nickel powder were mixed with calculated additions of compounds of the elements to be determined. The resultant graphs were found to be concurrent with those obtained with chemically analysed, melted samples. It was also found that graphs obtained by varying the weight taken of any one standard were concurrent with graphs obtained for constant weights of standards of varying element concentration.

Standardisation is thus reduced to the mechanical blending of one sample, and the necessity for chemical analysis is eliminated. It seems that, in the presence of silicon, the chemical form of the element analysed has no effect on its resultant line intensity.

RESULTS

By using the conditions outlined in Table IV studies have been made of the precision and accuracy of the technique.

PRECISION—

Several samples of a particular nickel-base complex alloy were used to establish calibrations for the elements arsenic, antimony, bismuth, tin, lead and silver. A further sample of this material was analysed sixteen times on the same day with the same photographic plate. The results obtained are shown in Table VII.

TABLE VII
ANALYTICAL PRECISION FOR HIGH TEMPERATURE NICKEL ALLOY

Element*	As	Sb	Bi	Sn	Pb	Ag
Content, per cent.	0.020	0.026	0.0009	0.012	0.0014	0.0030
Standard deviation	2.5×10^{-3}	2.4×10^{-3}	7.2×10^{-5}	1.4×10^{-3}	1.2×10^{-4}	3.4×10^{-4}
Coefficient of variation, per cent.	12.5	9.2	8.0	11.6	8.6	11.4

* The wavelengths of lines used are given in Table I, together with that of the helium reference line.

The mean precision, expressed as a coefficient of variation, is 10.2 per cent.

ACCURACY—

A sample of doped nickel powder was used to prepare calibration graphs in the presence of 10 mg of silicon. The weight of doped powder standard was varied to prepare graphs covering the appropriate element concentration range and the final weight adjusted to 40 mg (including 10 mg of silicon) by the addition of Specpure nickel turnings.

Samples were analysed by adding 10 mg of silicon to 30 mg of the sample in the graphite crucible, without mixing. The results obtained (averages of four exposures) are shown in Tables VIII, IX and X, together with accepted values.

DISCUSSION

The results shown in Tables VIII, IX and X were all obtained by using calibrations from a single blended powder standard. Similar accuracy was achieved for high alloy steels and a variety of materials used in their manufacture, including chromium, cobalt, ferro-molybdenum, nickel - niobium (40 + 60 per cent.), titanium and tungsten. In fact, the use of a blended nickel powder standard, together with the addition of silicon buffer to the standard and samples, will provide accurate results for most of the materials encountered in the high temperature alloy field.

TABLE VIII
ANALYSIS OF VARIOUS SAMPLES WITH CONSTANT TRACE-ELEMENT ADDITIONS

Sample No.	Material	Element concentration found, per cent.										
		Bi	In	Ga*	Sn	Pb	Tl	Sb	Zn*	Ag	Te*	As*
R3393	Nickel	0-0009	0-0010	0-001	0-006	0-0014	0-0014	0-0013	0-001	0-0011	0-001	0-01
	Hollow cathode	0-0012	0-0010	0-0012	0-006	0-0013	0-0016	0-0018	0-0009	0-0009	0-0012	0-014
R3394	Cobalt	0-0008	0-0011	0-001	0-006	0-0014	0-0004	0-0020	0-001	0-0010	0-001	0-01
	Hollow cathode	0-0010	0-0009	0-0013	0-006	0-0012	0-0006	0-0021	0-0007	0-0018	0-0014	0-012
R3395	Iron	0-0008	0-0008	0-001	0-007	0-0009	0-0008	0-0033	0-001	0-0010	0-001	0-01
	Hollow cathode	0-0010	0-0009	0-0019	0-007	0-0013	0-0010	0-0038	0-0008	0-0011	0-0011	0-013
R3396	Nickel 80%; chromium 20%	0-0009	0-0008	0-001	0-006	0-0014	0-0008	0-0016	0-001	0-0012	0-001	0-01
	Hollow cathode	0-0011	0-0009	0-0009	0-005	0-0012	0-0012	0-0018	0-0010	0-0010	0-0010	0-009
R3400	Nickel 40%; iron 40%; chromium 20%	0-0008	0-0009	0-001	0-006	0-0010	0-0008	0-0025	0-001	0-0012	0-001	0-01
	Hollow cathode	0-0011	0-0011	0-0012	0-006	0-0012	0-0010	0-0028	0-0009	0-0013	0-0012	0-010
R3401	Iron 50%; nickel 30%; cobalt 20%	0-0008	0-0009	0-001	0-007	0-0011	0-0007	0-0019	0-001	0-0011	0-001	0-01
	Hollow cathode	0-0009	0-0010	0-0014	0-006	0-0011	0-0010	0-0026	0-0007	0-0010	0-0011	0-010

*The "Accepted" values given are the nominal additions; all other elements were determined by spectrochemical methods.

TABLE IX
HOLLOW-CATHODE DISCHARGE ANALYSIS OF HIGH TEMPERATURE ALLOYS

Sample No.	Material	Element concentration found, per cent.										
		Bi	In	Ga*	Sn	Pb	Tl	Sb	Zn*	Ag	Te*	As*
R3385	Nickel-base alloy†	0-0001	0-0001	0-0002	0-009	0-0001	0-0001	0-0004	0-0001	0-0001	0-0001	0-01
	Hollow cathode	0-0002	0-0002	0-0003	0-011	0-0002	0-0002	0-0006	0-0001	0-0001	0-0002	0-0053
R3386	Nickel-base alloy†	0-0002	0-0002	0-0005	0-050	0-0002	0-0002	0-0009	0-0002	0-0002	0-0002	0-005
	Hollow cathode	0-0003	0-0003	0-0006	0-0056	0-0003	0-0003	0-0011	0-0002	0-0002	0-0003	0-0051
R3387	Nickel-base alloy†	0-0009	0-0009	0-002	0-0014	0-0009	0-0009	0-0048	0-001	0-0009	0-001	0-001
	Hollow cathode	0-0012	0-0011	0-0026	0-0015	0-0012	0-0011	0-0056	0-0010	0-0009	0-0013	0-0016
R3388	Nickel-base alloy†	0-0005	0-0005	0-001	0-0026	0-0005	0-0004	0-0019	0-0005	0-0005	0-0005	0-002
	Hollow cathode	0-0006	0-0006	0-0012	0-0025	0-0006	0-0006	0-0022	0-0004	0-0004	0-0007	0-0023

*The "Accepted" values given are the nominal additions; all other elements were determined by spectrochemical methods.

† Basic composition, per cent.: nickel 60, chromium 15, cobalt 15, molybdenum 5, titanium 2½, aluminium 2½.

TABLE X
ANALYSIS OF CERTIFIED STEEL STANDARDS

Sample No.	Material		Element concentration found, per cent.		
			Pb	Sn	As
SS13	Mild steel	Certificate value	0.003(0)*	0.06(5)	—
		Hollow cathode	0.0030	0.062	—
SS16	Mild steel	Certificate value	0.006(5)*	0.01(0)	—
		Hollow cathode	0.0062	0.010	—
SS32	Carbon steel	Certificate value	—	—	0.003
		Hollow cathode	—	—	0.0035
SS33	Carbon steel	Certificate value	—	—	0.070
		Hollow cathode	—	—	0.067

* Non-standardised element.

Analysis of low melting-point materials, such as copper, manganese or aluminium alloys, requires the blending of separate standards based on the particular matrix type encountered and, in general, produces inferior sensitivities, particularly for those elements with boiling-points close to those of the matrix components. The determination of elements whose boiling-points are higher than those of the matrix elements is impracticable by direct means.

TABLE XI
LIMITS OF DETECTION FOR HOLLOW-CATHODE EXCITATION

Limit of detection, p.p.m.	Element
≤0.01	Ag, Ca, Cd, In, Mg, Na
>0.01 to ≤0.1	Bi, Cu, Ga, Mn, Pb, Tl, Zn
>0.1 to ≤1.0	Ba, Ge, K, Sb, Sn
>1.0 to ≤10	As, Te

By using the conditions outlined previously, limits of detection for some elements have been determined for steels and nickel-base alloys, and are shown in Table XI. These limits refer to the optimum general procedure used, but it is obvious from the discussion on sensitivity that the limit for any particular element may be extended by reference to such factors as electrode geometry and gas pressure. The values in Table XI are estimates for direct examination, but the use of pre-concentration techniques may also be applicable, with consequent increases in sensitivity.

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REFERENCES

1. Paschen, F., *Annln Phys.*, 1916, **50**, 901.
2. —, *Sber. preuss. Akad. Wiss.*, 1928, **32**, 3.
3. —, *Annln Phys.*, 1923, **71**, 142.
4. McNally, J. R., Harrison, G. R., and Rowe, E., *J. Opt. Soc. Amer.*, 1947, **37**, 93.
5. Birks, F. T., *Spectrochim. Acta*, 1954, **6**, 169.
6. Berezin, I. A., and Aleksandrovich, K. V., *Zh. Analit. Khim.*, 1961, **16**, 613.
7. Berezin, I. A., *Zav. Lab.*, 1961, **27**, 859.
8. Falk, H., *Spectrochim. Acta*, 1965, **21**, 423.
9. Korovin, Y. I., and Lipis, L. V., *Optika Spektrosk.*, 1958, **5**, 334.
10. Ivanov, N. P., Nedler, V. V., and Andrikanis, E. N., *Zav. Lab.*, 1961, **27**, 836.
11. Pevstov, G. A., and Krasil'shchik, V. Z., *Zh. Analit. Khim.*, 1964, **19**, 1106.
12. Matic, J. S., and Pešić, D. S., *Revue Roum. Chim.*, 1965, **10**, 733.
13. —, —, *Appl. Spectrosc.*, 1968, **22**, 63.
14. Rosen, B., *Revue Univille Mines*, 1953, **9**, 445.
15. Webb, M. S. W., and Webb, R. J., *Analytica Chim. Acta*, 1965, **33**, 138.
16. —, —, *Ibid.*, 1966, **36**, 403.
17. Mitchell, K. B., *J. Opt. Soc. Amer.*, 1961, **51**, 846.
18. van Voorhis, C. C., and Shenstone, A. G., *Rev. Scient. Instrum.*, 1941, **12**, 257.
19. Mitchell, G. P., and Harris, C. I., *Proc. Soc. Analyt. Chem.*, 1965, 105.
20. Jaycox, E. K., *J. Opt. Soc. Amer.*, 1947, **37**, 159.
21. Balfour, B. E., Jukes, D., and Thornton, K., *Appl. Spectrosc.*, 1966, **20**, 168.

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