High-pressure Plasmas as Spectroscopic Emission Sources

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An account is given of the authors' preliminary work in the use of high-pressure plasmas as both spectrographic and flame-photometric emission sources. Two types of plasma sources are discussed, *viz.*, the d.c.-arc type and the high-frequency induction type; the latter, having no electrodes, produces little background emission. Tables of the order of detection for some metallic elements are given, but these are not absolute detection limits. The standard deviation obtained with calcium emission at 3933Å is given for both sources.

In the determination of calcium by flame photometry, a depression of the calcium emission occurs in the presence of phosphorus, and more markedly, aluminium, owing to the formation of stable compounds in the flame.[1] The interference of phosphorus can be overcome and that of aluminium diminished by raising the flame temperature. This has been done by injecting oxygen into an air - acetylene flame.[2] It was thought that if the flame temperature were raised even further, the interference of aluminium could be completely overcome and attention was turned to the possibility of using an oxy-cyanogen or a hydrogen - fluorine flame. These flames have been used,[3,4] but were considered too hazardous for general use. Atomic-hydrogen torches[5] and augmented flames[6] were briefly considered, but finally it was decided that d.c.-arc plasma jets offered an elegant approach to this problem.

Several types of these jets were built and operated, and then the apparent advantages of the high-frequency-heated plasma type over the d.c.-arc type, notably the freedom from electrode contamination, became of interest. Also, by this time a spectrograph had been acquired and interest in spectral sources received a fresh impetus. Work on high-frequency plasmas was therefore carried out concurrently with that on d.c.-arc plasmas.

The operating principles of these two sources are different from each other and are briefly described below. A more detailed description can be found in the literature.[7,8]

In the d.c.-arc plasma jet, a closed chamber contains at one end an anode (or cathode) and at the other end a cathode (or anode) that has a small opening in it. A coolant fluid (argon) is introduced tangentially through the chamber wall and swirls around the chamber and out of the cathode hole. When the arc is struck the coolant fluid cools the outer layers of the arc so giving a "thermal pinch" effect, which causes the arc column to contract. The resultant increase in current density gives a higher arc temperature, and the pressure generated leads to the ejection of extremely hot plasma through the cathode opening, where it appears as a flame-like jet. At higher operating currents, the arc suffers a further "pinch" effect called the "magnetic pinch" due to the self-induced magnetic field. For spectroscopic purposes the substance to be analysed is injected into the arc column and is carried out in the plasma flame.

In the high-frequency plasma torch, a stream of ionised gas (argon) contained in a circular quartz tube, surrounded by a coil carrying high-frequency alternating electric current, is heated by induction. Cold gas, being un-ionised, is not an electrical conductor and therefore the plasma torch must be externally initiated, which can be achieved by holding a carbon rod in the mouth of the quartz tube. The high-frequency field heats the carbon rod, which in turn heats and ionises the argon. Once the main discharge has started, the carbon rod is removed and the gas stream carries the ionised gas plasma down the tube away from the coil, where it emerges at the tube mouth as a "flame." To maintain the discharge, a portion of the ionised gas must be re-cycled. This is achieved by feeding the gas tangentially into the tube which causes a vortex, and the partial reduction in pressure at the centre of this causes some of the ionised argon to move back down the tube in the opposite direction to the main gas flow.

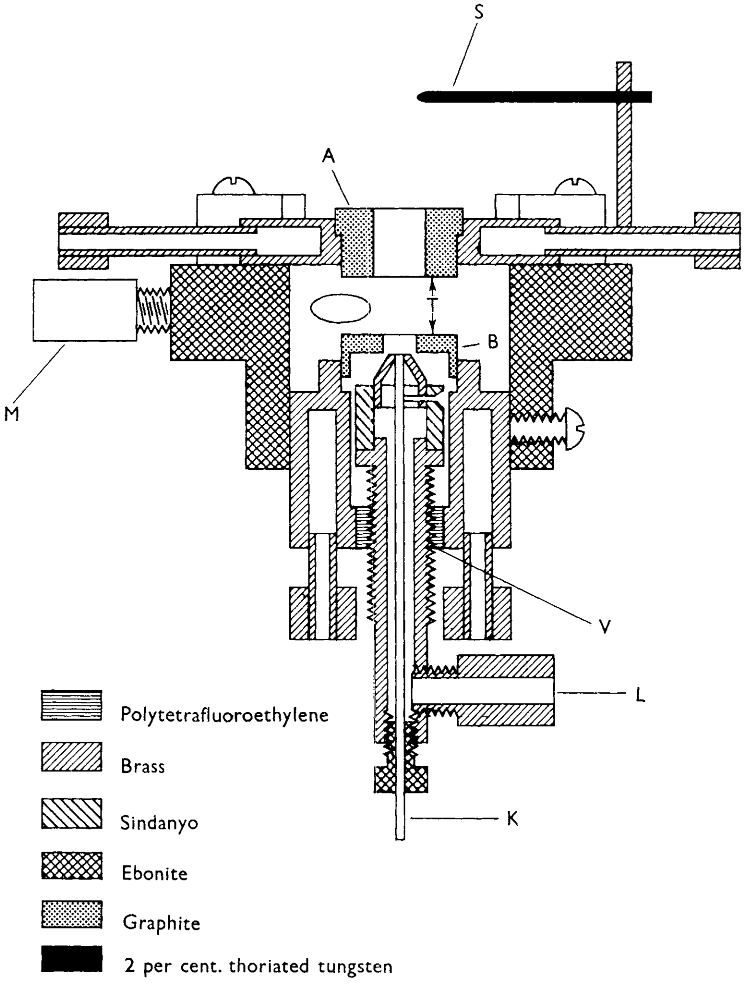
The quartz tube described in this paper is cooled by a secondary stream of argon passing over it. When fully coupled, the high-frequency plasma can be regarded as a transformer, the work coil being the primary and the ionised gas a one-turn secondary.

The factor limiting the maximum temperature of a combustion flame is the dissociation of the gases in the flame. These various dissociations consume an appreciable amount of the thermal energy released by the flame reaction, and thus prevent this energy being used to increase the gas temperature. The hottest flames are those whose combustion products are stable molecules with high dissociation temperatures. For example, the temperature developed by the reaction—

$$C_2N_2 + O_2 \rightarrow 2CO + N_2$$

is 4850° K.

In a thermal plasma, the gas is not heated by energy liberated in a chemical reaction, but by electrical energy. The electric field imparts kinetic energy to the electrons in the plasma, which then share this energy with plasma atoms and ions by colliding with them; as a result electrons, atoms and ions are in thermal equilibrium. The temperature of a thermal



A = Anode opening increased to 6 mm

B = Cathode, 8-mm opening, and projecting 1 mm either side of cooling-jacket

K = Capillary tube, 24 s.w.g. stainless steel

L = Argon inlet, 5 p.s.i., 5 litres per minute

M = Coolant-argon inlet, 2 p.s.i., 7 litres per minute

S = Stabiliser electrode, $\frac{1}{8}$-inch rod, 7 mm from top of cathode

T = 3-mm gap, 10-A d.c. arc, 230-V line voltage

V = Tapped polytetrafluoroethylene insulator

Fig. 1. Diagram of modified Margoshes and Scribner plasma jet

plasma is not limited by the dissociation temperature of the gas, in fact it must be higher than the temperature at which the gas ionises, since the electrical conductivity of the gas depends upon the number of electrons and ions. The temperature of a thermal plasma generally lies between the temperatures required to bring about 10 per cent. and 50 per cent. ionisation. From this it can be seen that the temperature of a plasma must be higher than that of a normal flame. The limit set upon plasma temperatures is the temperature at which increasing ionisation is countered by thermal expansion and the conductivity of the plasma no longer increases with temperature.

D.C.-ARC PLASMA JETS

Our first experiments on the application of this type of source to spectroscopic analysis were carried out with a modified version of the tungsten-electrode plasma jet used for chemical synthesis by Stokes and Knipe.[9] The polytetrafluoroethylene insulating gasket was replaced with polypropylene, and the coolant gas (argon) was fed through a gasket with a $\frac{7}{16}$-inch bore tube. The coolant gas at a rate of 7 litres per minute was supplied from the expansion chamber of a Unicam atomising unit so that a liquid sample could be fed to the plasma jet as an aerosol. An adjustable $\frac{1}{8}$-inch, 2 per cent. thoriated tungsten rod was connected to the tungsten insert electrode (used as the cathode) to act as a stabiliser electrode. The use of a stabiliser electrode improved the operation of the assembly. The plasma jet was powered from a rotary convertor at 22 amps d.c., and was initiated by shorting the two electrodes.

However, this type of plasma generator was found to be too unstable for use with a non-integrating type of flame spectrophotometer, such as the Unicam SP900. Further, it was found that sample-to-sample contamination occurred because of condensation in the arc chamber, and that tungsten emission from the electrodes gave high background readings.

With the experience gained from these experiments it was decided that it was necessary to use a plasma jet specifically designed for spectroscopic analysis with direct injection of liquid samples into the plasma jet.

Such a plasma generator had already been used by Margoshes and Scribner.[10] A similar generator was built, and with the modifications shown in Fig. 1 it provided a stable spectrographic source. The modifications were made to improve its operation and to permit the jet to be used with a d.c. source limited to a maximum of 15 amps output.

Attempts to use this unit as the emission source on the Unicam SP900 flame spectrophotometer were unsuccessful because of the instability introduced by flare from the stabiliser electrode, although Webb and Wildy[11] used this type of plasma jet with great success, by screening the stabiliser and using an integrating flame photometer incorporating an additional photomultiplier tube to monitor the background interference.

Some preliminary experiments were carried out by using this plasma jet with aqueous solutions on a Hilger large-quartz spectrograph. The plasma-jet assembly was mounted in the electrode holders of a Hilger FS55 spark stand so that all the usual adjusting controls could be used for alignment.

TABLE I

ORDER OF THE LEVELS OF DETECTION FOR THE D.C.-ARC PLASMA JET

Species	Spectrum line, Å	Concentration of aqueous solution, p.p.m.	Percentage transmission	
			line + background	background
Ca^{II}	3933·666	2	53·7	61·6
Sr^{II}	4077·714	5	49·0	60·3
Ba^{II}	4554·042	5	66·1	69·2
Al^{I}	3961·527	100	42·7	50·1
Mn^{II}	2576·104	10	77·6	95·5
Cu^{I}	3247·540	10	61·7	74·1
Cr^{II}	2835·633	20	72·4	89·1
Mg^{II}	2795·530	1	77·6	91·2
Co^{I}	3453·505	50	54·9	57·5

The results obtained from the preliminary experiments are shown in Tables I and II.

Table I shows the order of the levels of detection obtained. Ilford N.30 plates were used, an exposure of 30 seconds was given with a slit width of 0·01 mm. The atomising rate of sample to the plasma was 0·25 ml per minute. The quartz optical system was used, and the source was focused on the slits so that the top of the cathode and the tip of the stabiliser electrode were excluded.

Table II gives the stability of the d.c.-arc plasma jet as a source. Ilford N.30 plates were used, an exposure of 30 seconds was given with a slit width of 0·015 mm and slit height of 3 mm. The quartz optical system was used with the source focused on the slit. The source was run continuously, and a solution containing 20 p.p.m. of calcium was aspirated at 0·25 ml per minute whilst the 10 exposures were made. The plate was developed in a dish with P.Q. Universal developer for three minutes at 20° C. The plate was calibrated by using a rotating stepped sector and a 3-amp iron arc. The standard deviation of the values for the percentage transmission given in Table II was calculated by using the root mean square method and by assuming normal distribution. The standard deviation for percentage transmission for calcium 3933 is ±0·12, *i.e.*, the coefficient of variation is 4·5 per cent. Considering the high level of background density in this wavelength region, the source stability indicated by the above figure is extremely good.

TABLE II

STABILITY OF THE D.C.-ARC PLASMA JET

Exposure number	Percentage transmission of Ca 3933Å, *plus* background	Percentage transmission, background	Percentage transmission of Ca 3933Å, corrected for background
1	1·30	12·58	2·72
2	1·30	13·18	2·70
3	1·30	13·18	2·70
4	1·45	14·45	2·75
5	1·41	13·80	2·82
6	1·30	13·80	2·58
7	1·30	14·45	2·51
8	1·30	14·45	2·51
9	1·41	14·79	2·75
10	1·41	14·12	2·82

TEMPERATURE OF THE SOURCE—

By using the lines for calcium at 3933·666Å and 4226·728 Å at the 20 p.p.m. of calcium level, the degree of ionisation of the calcium in the plasma jet was found to be 77 per cent. By using the Saha equation,[15] this degree of ionisation indicates an electron temperature of approximately 9500° K.

OPERATION OF THE PLASMA-JET UNIT—

The unit is simple to operate and has been run for periods of up to 30 minutes.

No carry-over contamination between samples was found if a 30-second wash with deionised water was made between exposures. Since the plasma-jet column and the sample spray do not touch the electrodes during operation, the electrodes can be used for many exposures. Owing to the burning of the top electrode (cathode) during the initiation of the plasma, this electrode has to be replaced at intervals. If spark initiation of the unit were used, this troublesome erosion of the cathode could no doubt be avoided.

Since the unit uses aqueous samples at a rate of only 0·25 ml per minute, an exposure of 30 seconds with a pre-spray time of 30 seconds will use only 0·25 ml of sample.

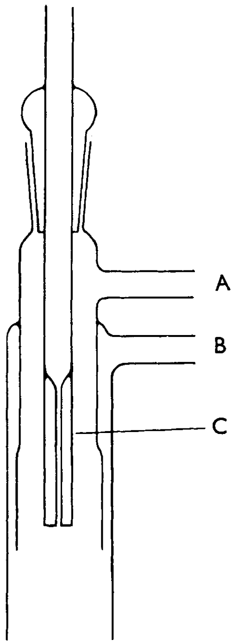
If the atomiser is used under the same operating conditions, the atomising rate for organic solvents such as alcohol, acetone, diethyl ether, chloroform and carbon tetrachloride will be much higher; if necessary the uptake of sample can be reduced by dropping the atomiser pressure or by adjusting the position of the atomiser needle. The above-mentioned solvents have been sprayed into the plasma jet quite satisfactorily by using the same operating conditions as for aqueous solutions.

Attention was now turned to high-frequency thermal plasmas, since it had not been possible to use the d.c. plasma jet on the flame photometer.

HIGH-FREQUENCY THERMAL PLASMA TORCH

The initial experiments were carried out on argon plasmas in single silica tubes with a 4·5-Mc/s, 1·0-kW induction-heating generator. These experiments indicated that powers greatly in excess of 1·0 kW were necessary to maintain a stable source at this frequency and be capable of exciting aqueous aerosols. Ultimately, a 2·5-kW dielectric-heating generator operating at 36 Mc/s and modified to work with inductive coupling was used.

The torch cell evolved is a modified form of the type used by Reed[12] in his experiments on the growth of refractory crystals. The cell with an aerosol injector fitted is shown in Fig. 2, and consists basically of two concentric clear silica tubes with individual gas-entry tubes, A and B, joined tangentially to the main tubes. The cell also carries a silica B14 socket, which takes the sample injectors for gases, vapours, aerosols, liquids, powdered solids and slurries. The sample injectors are all made of Pyrex glass and are sufficiently separated from the plasma to prevent their melting.



A = Plasma-argon tangential inlet
B = Coolant-argon tangential inlet
C = Pyrex-glass aerosol injector

Fig. 2. Diagram of the high-frequency plasma-torch silica cell

The plasma torch was run at 1·5-kW output power. The plasma gas used was argon at a flow-rate of 5 litres per minute via side-tube A, with a coolant gas (argon) flow-rate of 17 litres per minute via side-tube B. The plasma was coupled to the generator output via a work coil consisting of $3\frac{1}{2}$ turns of $\frac{1}{4}$-inch o.d., $\frac{3}{32}$-inch i.d. copper tube. The overall diameter of the coil was $1\frac{3}{4}$ inches, and the separation between turn centres was $\frac{5}{8}$ inch. The live coil was placed nearest the open end of the tube just above the plasma tube. Initiation was by carbon rod.

Since this paper was read before a Joint Meeting of the Society for Analytical Chemistry and The Sheffield Metallurgical Association, in October 1963, descriptions of other high-frequency plasma torches have come to our attention.[13,14] The torch described in this paper differs from these, in that it uses an argon plasma, has no central electrode and is capable of exciting aerosols, liquids or powders. The sample path is of glass or quartz, and contamination of sample is less likely than in any other type of torch so far described in the literature. The radiation from the sample is produced in a "tail-flame" region remote from the main body of the plasma. The torch can be so aligned that the radiation from the main plasma does not enter the spectrograph or monochromater slit, and apart from the OH band system no intense background spectrum is produced.

The torch produces a flame-like plasma $1\frac{1}{4}$ inches long, $\frac{3}{4}$ inch in diameter and annular in form, *i.e.*, it has a hole or low-temperature region in its centre. The sample is injected through this low-temperature region, and if the radiation produced by the sample is in the visible range of the spectrum, a coloured "tail flame" is produced downstream of the main plasma.

The series of experiments carried out on the d.c.-arc plasma jet were repeated with the high-frequency plasma torch as the source on a Hilger large-quartz spectrograph and a Unicam SP900 flame spectrophotometer. The results obtained are given in Tables III and IV. These figures are intended as an indication of the order of sensitivity available with an aerosol injector, which delivers about 10 per cent. of the sample to the plasma. If the torch is used with direct injection of liquids and especially with powders, the levels of photographic detection should be improved by a factor of about ten, and better than this when photomultiplier detection is used.

Table III shows the order of levels of detection obtained. Ilford N.30 plates were used with an exposure of 60 seconds, and the slit width was 0·03 mm. The rate of atomisation into the cyclone chamber of the aerosol injector was 2·5 ml per minute. The quartz optical system was used and the "tail flame" of the plasma flame was focused on the slit.

The background transmission of the N.30 plates for the region 2,300 to 5,000Å is 99·5 to 99·8 per cent. under the exposure conditions given in Table III. Therefore, with such favourable background conditions the figures can be improved by increasing the exposures or by using more sensitive plates. Table IV shows the stability of the high-frequency plasma torch. Ilford N.30 plates were used with an exposure time of 30 seconds. The slit width was 0·01 mm, and the slit height was 3 mm. With the source in continuous operation, a solution containing 100 p.p.m. of calcium was aspirated at 2·5 ml per minute into the cyclone chamber of the aerosol injector, and the ten exposures were made. The quartz optical system was used with the "tail-flame" region focused on the slit. The plate was developed in a dish with P.Q. universal developer for 3 minutes, and calibrated by using a rotating stepped sector and a 3-amp iron arc. No background correction was carried out on the results shown in Table IV because the transmission was 99·5 to 99·8 per cent.

TABLE III

ORDER OF THE LEVELS OF DETECTION FOR THE HIGH-FREQUENCY PLASMA TORCH

Species	Spectrum line, Å	Concentration of aqueous solution, p.p.m.	Percentage transmission	
			line + background	background
Ca^{II}	3933·666	1	85·1	99·5
Al^{I}	3961·527	50	83·2	99·3
Mn^{I}	4030·755	10	89·1	99·5
Cu^{I}	3247·540	10	81·3	99·8
Cr^{I}	4254·366	20	87·1	99·3
Mg^{II}	2795·530	5	85·1	99·3
Ni^{I}	3414·765	5	77·6	99·5
Co^{I}	3453·505	100	93·3	99·3

TABLE IV

STABILITY OF THE HIGH-FREQUENCY PLASMA TORCH

Exposure number	Percentage transmission for Ca 3933 Å	Percentage transmission for Ca 4226 Å
1	33·72	36·31
2	34·20	36·65
3	34·35	37·15
4	35·98	38·38
5	39·44	40·18
6	36·99	37·32
7	39·09	41·68
8	39·00	40·55
9	36·81	39·26
10	39·81	40·72

The standard deviation of the values for percentage transmission given in Table IV was calculated by using the root mean square method and by assuming normal distribution. Thus for the calcium 3933 Å line, the standard deviation of the percentage transmission was ±2·3, *i.e.*, the coefficient of variation was 6·2 per cent., and for the calcium 4226 Å line, the standard deviation of the percentage transmission was ±1·9, *i.e.*, the coefficient of variation was 4·9 per cent. These figures indicate a high degree of source stability.

TEMPERATURE OF THE SOURCE—

As for the d.c.-arc plasma jet, the approximate temperature of this source was again calculated by using the degree of ionisation of calcium at the 20 p.p.m. level.

The source is composed of three more or less distinct regions, *viz.*, the extremely hot plasma region inside the cell in the maximum field of the work coil (temperature, 12,000 to 15,000° K), the cooler plasma region, which is outside the cell, and the "tail-flame" region. Since most of the work done here has been in the "tail flame," the temperature was measured in this region. Thus for 20 p.p.m. of calcium, the degree of ionisation was approximately 46 per cent. This degree of ionisation indicates a sample electron temperature of 8000° K.

OPERATION OF THE HIGH-FREQUENCY THERMAL PLASMA TORCH—

The source is simple to operate, no electrodes are involved and once the unit has been correctly set up the quartz cell is not affected by the plasma flame.

The torch has been operated continuously with an argon plasma for periods of 8 hours without any difficulty.

Most of the preliminary work has been done with an indirect atomiser and an aerosol feed to the plasma. However, direct injection into the plasma of liquids (aqueous and organic), powdered solids and slurries has also been carried out. No quantitative work with direct injection has as yet been carried out, but the "tail flame" produced is extremely intense and appears to be quite stable.

HIGH-FREQUENCY PLASMA TORCH USED ON A FLAME SPECTROPHOTOMETER—

The "tail-flame" region of the torch was roughly aligned on the optical axis of a Unicam SP900 flame spectrophotometer, no lens or mirror being used.

The reproducibility of the calcium line at 422·7 mμ, as plotted on a chart recorder over a period of 1 hour (20 scans of the calcium line being taken in this period), was found to be ±2 per cent. at the 10 p.p.m. level.

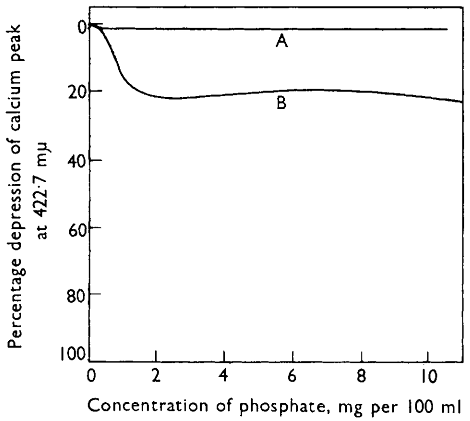


Fig. 3. Graph showing release from phosphate interference on 12 p.p.m. of calcium with a high-frequency torch. Curve A, high-frequency plasma torch; curve B, air - acetylene flame

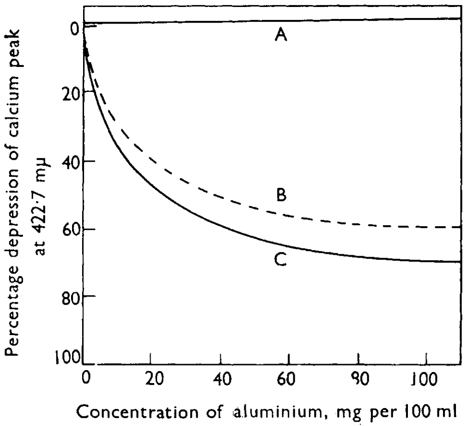


Fig. 4. Graph showing release from aluminium interference on 30 p.p.m. of calcium with a high-frequency plasma torch. Curve A, high-frequency plasma torch; curve B, oxygen-rich air - acetylene flame; curve C, air - acetylene flame

As anticipated, the higher excitation energy available overcame the depressive effects mentioned in the introduction. Figs. 3 and 4 show this release from interference from phosphate and aluminium ions, respectively, on the calcium emission at 422·7 mμ. An indication of the increased sensitivity possible by using the high-frequency plasma torch is shown in Table V. The figures given in Table V are merely comparative, and should not be taken as detection limits.

TABLE V: COMPARISON OF THE HIGH-FREQUENCY PLASMA TORCH AND THE AIR - ACETYLENE FLAME ON THE UNICAM SP900 SPECTROPHOTOMETER

Gain, 6·2; slit width, 0·08 mm; aqueous solutions

Element	Wavelength, mμ	Detection in—	
		air - acetylene flame	high-frequency plasma torch
Mercury.. ..	253·6 (atomic line)	10,000 p.p.m. give 5 galvanometer divisions' deflection	50 p.p.m. give 5 galvanometer divisions' deflection
Zinc	334·5 (atomic line)	10,000 p.p.m. cannot be detected	50 p.p.m. give 5 galvanometer divisions' deflection
Aluminium ..	484 (oxide band system)	200 p.p.m. give 5 galvanometer divisions' deflection	—
Aluminium ..	396 (atomic line)	1000 p.p.m. give 5 galvanometer divisions' deflection	20 p.p.m. give 5 galvanometer divisions' deflection

CONCLUSIONS

Our experience with these sources shows them to have advantages that may be conveniently summarised under two headings.

FLAME PHOTOMETRY—

The plasma source has a high degree of stability, has the ability to overcome depressive interference effects caused by the formation of stable compounds, is capable of exciting several elements that are not excited in orthodox chemical flames, and gives increased sensitivity of detection.

SPECTROGRAPHY—

The plasma source is far simpler to operate than the conventional arc and spark methods, especially in solution and liquid analysis, and gives the high degree of stability associated with the a.c. spark combined with the sensitivity of the d.c. arc.

Particular advantages of the high-frequency plasma torch are the lack of electrodes, which gives freedom from contamination, and the extremely low background produced.

The ability to inject powdered samples directly into the plasma, over a period of time, overcomes the problem of sample inhomogeneity and allows longer exposures to be given than with usual powder techniques, with consequent increase in sensitivity. It is hoped to publish shortly some further basic work on the high-frequency plasma torch itself, and some actual analytical methods, some absolute detection limits and results obtained with this source.

We thank Mr. D. I. Spash and Mr. M. R. Yates of Radyne Limited* for their technical assistance and for the loan of high-frequency generators. We also thank Mr. C. L. Brierley for the construction of apparatus.

* Joint patent applications have been made by Messrs. Albright & Wilson (Mfg) Ltd. and Radyne Ltd., for this method and apparatus for exciting substances to emit radiation.

REFERENCES

1. Schuhknecht, W., and Schinkel, H., *Z. Anal. Chem.*, 1958, **162**, 266.
2. Greenfield, S., and Berry, C. T., *in* "Analysis of Calcareous Materials," *S.C.I. Monograph No.* 18 Society of Chemical Industry, London, 1964, p. 259.
3. Baker, M. R., and Vallee, B. L., *J. Opt. Soc. Amer.*, 1955, **45**, 773.
4. Priest, H. F., and Grosse, A. V., *J. Ind. Eng. Chem.*, 1947, **39**, 431.
5. Langmuir, I., *Science*, 1925, **62**, 463.
6. Karlovitz, B., *International Science and Technology*, June, 1962, 36.
7. Giannini, G. M., *Scientific American*, 1957, **197**, 80.
8. Reed, T. B., *International Science and Technology*, June, 1962, 42.
9. Stokes, C. S., and Knipe, W. W., *J. Ind. Eng. Chem.*, 1960, **52**, 287.
10. Margoshes, M., and Scribner, B. F., *Spectrochim. Acta*, 1959, (2), 138.
11. Webb, M. S. W., and Wildy, P. C., *Nature*, 1963, **198**, 1218.
12. Reed, T. B., *J. Appl. Phys.*, 1962, **32**, 2534.
13. Mavrodineanu, R., and Hughes, R. C., *Spectrochim. Acta*, 1963, **19**, 1309.
14. West, C. D., and Hume, D. N., *Anal. Chem.*, 1964, **36**, 412.
15. Ahrens, L. H., and Taylor, S. R., "Spectrochemical Analysis," Second Edition, Pergamon Press, Oxford, London, New York and Paris, and Addison-Wesley Publishing Company, Inc., Reading, Mass., and London, 1961, p. 24.

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