A two-jet plasmatron for the spectrochemical analysis of geological samples

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A two-jet plasmatron for the spectrochemical analysis of geological samples

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Abstract—The analytical possibilities with a two-jet plasmatron with non-consumable electrodes have been investigated. Large amounts of easily ionised additives present in the plasma enhance atom line intensities of trace elements, the effect being greater the lower the ionisation potential of the element but the effect on ion line intensities is not significant. The temperature of the plasma is only slightly affected by the ionisation potential of the substance introduced into the plasma.

Analytical errors caused by variations in the matrix and mineralogical composition of samples are of the same order as the random error of analysis. The analysis of different types of rock samples can be made using a single standard procedure giving a relative standard deviation of 4–6 % and detection limits between 10^{-5} and 10^{-7} %. A feature of the analytical method is the direct analysis of solid samples.

1. Introduction

Spectral analysis of complex geological samples of widely varying chemical and mineralogical composition often presents serious difficulties. Variations in the basic composition of samples are sometimes unknown and matching of the samples to corresponding standards is impossible. During the excitation of spectra in conventional arc sources these variations in the composition of the samples may affect the plasma temperature, the ionisation and chemical processes as well as the conditions of mass transfer in the source, all of which can lead to analytical errors. These errors can be serious and it would be of advantage to use an excitation source whose excitation conditions are virtually independent of sample composition. One such source is the jet plasmatron.

At present various types of arc plasmatron are available [1–3]. They are useful in the analysis of solutions which are introduced into the electrode gap in the form of aerosols carried by a carrier gas. The chemically reactive medium formed in the discharge zone as a result of the introduction of the sample leads to the corrosion and eventual destruction of the electrodes and thus to the malfunction of the plasmatron.

We have described [4] the construction and spectroscopic properties of a plasmatron with non-consumable electrodes. Samples to be analysed were introduced to the exterior of the plasma jet and therefore were not involved in the plasma formation processes.

A two-jet plasmatron with non-consumable electrodes appears to be a promising tool for spectral analysis [5]. It is more powerful than similar multi-jet plasmatron (100 A, 10 kW) and thus provides the opportunity of introducing not only solutions but also powders to the region between the two plasma jets outside the electrode assemblies. This paper describes the analytical properties of this plasmatron in the spectrochemical multi-element analysis of powders of complex composition such as rocks, ores and minerals.

2. Instrumentation

2.1. *Plasmatron*

The plasmatron is shown schematically in Fig. 1a. It consists of anode and cathode ports placed at an angle to each other. Each port has an electrode and three water-cooled copper

[1] L. E. Owen, *Appl. Spectrosc.* **15**, 150 (1961).
[2] E. Kranz, *Proc. 14th Coll. Spectr. Int.*, Debrecen, 1967, p. 697. Hilger, London (1968).
[3] S. E. Valente and W. Q. Schrenk, *Appl. Spectrosc.* **24**, 197 (1970).
[4] I. G. Yudelevich and A. S. Cherevko, *Spectrochim. Acta* **31B**, 93 (1976).
[5] V. S. Engelsht, K. U. Urmanbetov and Zh. Zh. Zheenbajev, *Zav. Lab.* **42**, 174 (1976).

discs separated from each other by rubber rings forming a nozzle. The cylindrical cathode made of thoriated tungsten, has a long consumable portion which is screwed into the copper holder. The anode is made of copper.

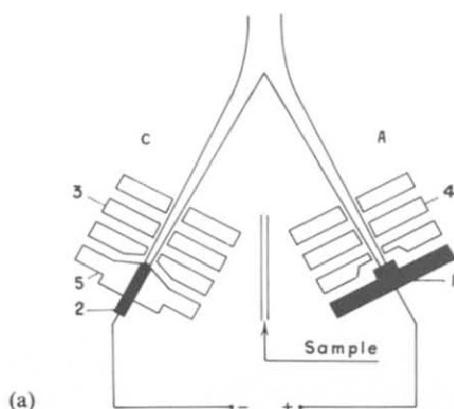The electrode protecting gas, argon, passes between the electrodes and the first copper disc

Fig. 1. (a) Schematic representation of the plasmatron: (1) anode, (2) cathode, (3, 4) diaphragms, (5) cathode holder; (b) the plasmatron in operation.

and the plasma support gas (air, argon, hydrogen, etc.) between the other discs. A photograph of the plasmatron in operation is shown in Fig. 1b.

2.2. Power supply

A standard rectifier was used as the power supply. To initiate arcing between the two electrodes a special start-up device is used, which is based on the principle of consecutive elongation of the arc along the cascade of copper discs. The merging of the two plasma jets above the electrodes produces a plasma flow with a velocity of $20 \, \text{m s}^{-1}$.

2.3. Sample introduction

The analyte, as a powder in a gas stream under pressure is injected between the two plasma jets as shown in Fig. 1a using a special device in which the powders are dispersed into the gas stream using a high frequency discharge. A natural vacuum is formed where the jets merge and this promotes the penetration of the sample into the central high temperature regions of the plasma. The amount of sample required for each analysis is 300 mg.

2.4. Operating conditions

2.4.1. *Particle size of the sample.* The particle size of the sample was about $5 \, \mu m$ and corresponds to the diameter for which virtually all of the sample is volatilised by the plasma [4]. This particle size was obtained using a semi-automatic vibrating attrition mill [6]. To ensure that the mill did not contaminate the sample small portions of "dirt" in the mill were analysed using atomic absorption spectrophotometry.

2.4.2. *Plasmatron.* The electric current used was 80 A and the consumption of the support gas, argon in this instance, was about $5 \, \text{l min}^{-1}$ resulting in a plasma of some 20 cm in length. The gas that carried the sample was argon.

2.4.3. *Spectrograph.* Spectra were obtained using a diffraction spectrograph with a grating with 600 lines mm^{-1} giving a reciprocal linear dispersion of $4 \, \text{Å mm}^{-1}$.

3. EXPERIMENTAL AND RESULTS

3.1. Analytical characteristics

3.1.1. *The effect of easily ionised additives on intensities of analytical lines.* We have studied the effect of easily ionised elements on the line intensities emitted by elements in the plasma formed by the two-jet plasmatron as follows:

Sample mixtures were prepared by mixing compounds of the elements Be, Sb, Sn, Pb, Ni, Bi, Cr, Ga, Mo, V, Zr, Ti, Y, Yb, Nb, La, Sc and Mn in trace amounts to each of two matrices consisting of (i) pure graphite powder and (ii) a 3:1 mixture a graphite powder and sodium fluoride respectively. The spectral line intensities emitted by these elements, which display a wide range of physical and chemical properties, were measured at distances of 5, 15 and 25 mm below the intersection of the two plasma jets. The ratio $F = I/I_0$, where I_0 is the intensity obtained with the pure graphite matrix and I that obtained with the matrix containing 25% NaF, was used as an indicator of the effect of NaF on the line intensities. The results obtained for the background corrected line intensities for vanadium are shown in Fig. 2. The other elements displayed a similar behaviour. Figure 3 shows the variation in the value of F for atom lines of ten of the elements when present in the samples at a concentration of 0.0001%.

These figures clearly show that:

(i) The intensity of both atom and ion lines for small amounts of additives can be considered maximum close to the merge of the two jets. As the concentration of the atoms in the plasma increases, the intensity maximum shifts slightly in the direction of the flow.

(ii) The intensities of atom lines increase with the addition of NaF into the plasma and the plasma region from where these lines are emitted becomes larger. It was found that this effect became more pronounced as the concentration of the analyte in the plasma decreased.

(iii) The effect of easily ionised additives on the intensities of atom lines is greater the lower the ionisation potential of the impurity elements. For the elements Sb and Bi with high ionisation potentials practically no effect was observed.

[6] I. A. KOPEYKIN, Semi-automatic vibrational mill for rock samples. Pat. USSR, N 290217, Invent. Bull. No. 27 (1970).
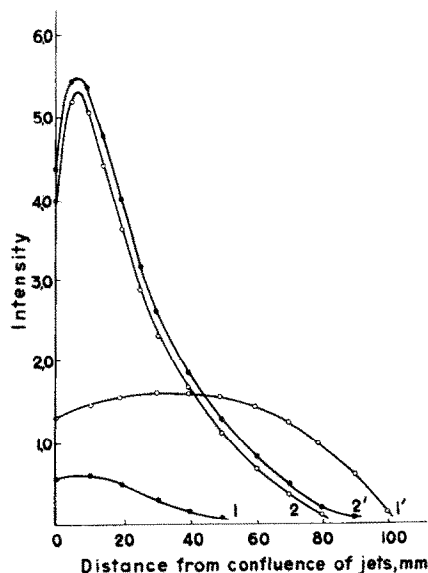
Fig. 2. Axial distribution of atom (1, 1') and ion (2, 2') line intensities of vanadium without (o) and with 25% NaF (o). V I 318,54 nm; V II 310.23 nm.
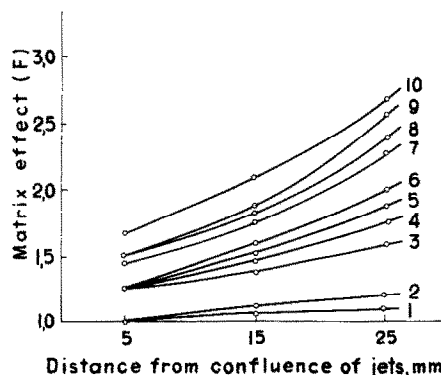

Fig. 3. Dependence of the matrix effect expressed in terms of F (see text) on the matrix composition.
(1) Be I 332.13 nm, (2) Sb I 259.81 nm, (3) Bi I 306.77 nm, (4) Pb I 283.31 nm, (5) Sn I 317.50 nm, (6) Ni I 305.05 nm, (7) Mo I 317.07 nm, (8) Ga I 294.36 nm, (9) Cr I 302.16 nm, (10) V I 318.54 nm.

(iv) The lower the ionisation potentials of the impurities, the larger the effect of easily ionised additives on the intensities of atom lines as one moves away from the point where the jets merge.

(v) The value of F (expressing the matrix effect) remains unchanged or decreases slightly within the range 1.0–0.9 for the ion lines of the elements investigated.

It is clear therefore that for analytical purposes the best region of the plasma is that near the intersection of the two plasma jets, i.e. where the effect of the composition of the matrix is a minimum and where the ion-line intensity is a maximum. Under the operating conditions described this position is about 7 mm from the point of intersection of the two plasma jets.

3.1.2. *The effect of the mineral composition of the samples on the intensities of analytical lines.* As shown in the literature the results of spectral analysis of various geological samples depend not only on interference effects related to the plasma characteristics but also on the mineral forms of the samples. When using methods involving the continuous introduction of samples into the plasma errors caused by these changes may reach between 50 and 100%.

To study the magnitude of this effect when using the two-jet plasmatron a series of standard samples were prepared by adding equal amounts of tungsten, in the form of wolframite or scheelite, and boron, in the form of tourmaline, ludwigite or datolite to SiO_2. Other samples such as diorite, bauxite, porphyrite, diabase and granite, which had already been analysed for Ti, Fe and Al, were also used in this study. The samples were diluted 1:1 with boron-free graphite powder to which 0.002% Pd had been added as an internal standard. The optimum position 7 mm below the intersection of the jets
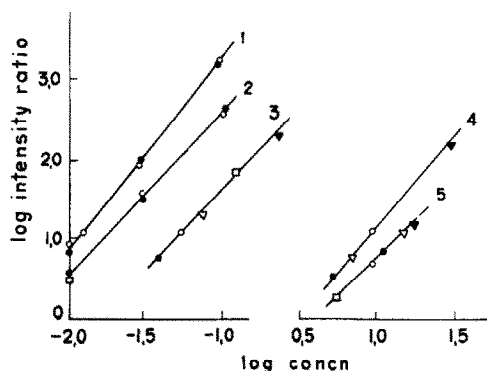
Fig. 4. Calibration curves (log intensity ratio of analysis line and reference line vs concentration) for W I 429.46 nm (1): wolframite (●), scheelite (o); B I 249.68 nm (2): tourmaline (●), ludwigite (o), datolite (□); Ti II 308.8 nm (3): granite (●), porphyrite (Δ), diorite (o), diabase (□), bauxite (▲); Fe I 301.62 nm (4): granite (●), porphyrite (Δ), diorite (o), bauxite (▲); Al I 308.22 nm (5): diabase (□), granite (●), diorite (o), porphyrite (Δ), bauxite (▲).

were projected onto the slit of the spectrograph and the spectra were photographed. Figure 4 gives the analytical calibration curves for W, B, Ti, Fe and Al obtained using these diverse samples. It can be seen from this figure that the mineralogical composition has virtually no effect on the relative line intensities and therefore on analytical results.

3.1.3. *The estimation of detection limits.* The detection limits of 20 elements were estimated using a procedure allowing the simultaneous determination of all the elements [7]. The 3σ criterion was used.

Artificial standards in a granite matrix were used as well as natural rock samples with known concentrations of trace elements, the latter being diluted with granite powder to bring the concentration of the elements into the 10^{-5}–10^{-7} % range. The estimated detection limits are shown in Table 1, which includes the detection limits obtained using the single jet plasmatron described in Ref. [4] for comparison purposes. The Table shows that the detection limits are lower for the two-jet plasmatron and in some instances are lower by more than an order of magnitude.

Table 1. Detection limits (%) of twenty elements

Element	Spectral line (nm)	Two-jet plasmatron	One-jet plasmatron [4]
Bi	306.8	1×10^{-5}	3×10^{-5}
Be	313.0	2×10^{-7}	2×10^{-7}
Cr	302.2	8×10^{-6}	9×10^{-5}
Co	345.3	3×10^{-6}	3×10^{-5}
Ga	294.4	5×10^{-6}	7×10^{-5}
Mo	317.0	2×10^{-5}	6×10^{-5}
Ni	341.5	4×10^{-6}	1×10^{-5}
Pb	283.3	8×10^{-5}	1×10^{-4}
Sb	259.8	2×10^{-4}	1×10^{-4}
Nb	316.3	2×10^{-5}	3×10^{-4}
Sc	335.4	2×10^{-6}	5×10^{-5}
Y	321.7	8×10^{-7}	6×10^{-5}
Sn	284.0	2×10^{-5}	5×10^{-5}
Mn	294.9	3×10^{-6}	3×10^{-5}
Yb	328.9	5×10^{-7}	8×10^{-6}
V	310.2	2×10^{-6}	
	318.5		3×10^{-5}
Ti	308.8	1×10^{-6}	5×10^{-6}
La	324.5	7×10^{-6}	6×10^{-5}
Zr	313.7	2×10^{-5}	
Ce	320.2	3×10^{-4}	

[7] A. I. KUZNETSOVA and Y. D. RAICHBAUM, *Zab. Lab.* **23**, 1076 (1970).

3.1.4. *The comparison of random errors of analysis obtained with the two-jet plasmatrons and with an a.c. arc.* It was of interest to determine the total random error and the magnitude of the main components of this error when using the two-jet plasmatron and to compare them with those obtained when using an a.c. arc as a source [8]. The total random error was assumed in both instances to consist of only two main components:

(i) The instrumental error, σ_r, which is a measure of the scattering of the results caused by random variations in the introduction of the sample, in the operation of the source, in the photometry of the signals, etc., and

(ii) The sample error, σ_c, which is a measure of the scatter of the analytical results caused by the variations in the matrix and in the mineralogical composition of the samples.

Four groups of natural rock samples corresponding to the mineral compositions of granadiorite, amphibolic syenite, diabase and harzburgite respectively were analysed using the two-jet plasmatron and an a.c. arc. Each group contained 3 different samples with known concentrations of the trace elements Be, Co, Cr, Ga, Mn, Mo, Nb, Ni, Pb, Sc, Sn, Ti, V, Zr, La, Y and Yb. Each sample was split into two portions making an overall total of 24 samples.

To normalise the results and thus obtain a uniform dispersion, samples differing in the percentage of the estimated components by less than 30 % were included in one group. Then the ratio of the analytical result to the actual concentration in the sample $(C_1 : C_0)$ was used. Using this ratio the skewness and excess coefficients of the distribution were 1.8 and 2.2 respectively, which meant that analysis of variance techniques could be used to obtain σ_r and σ_c. The results were processed according to the normal scheme of analysis of variance [12]. The systematic error, d, was calculated assuming that, if the ratio $C_i : C_0$ was equal to unity, then the systematic error was zero, i.e. $d = (1 - C_i : C_0) \times 100\%$. The significance of the deviation of d from zero was checked using Student's t criterion.

The results of the analysis of variance for the individual elements using both excitation sources are given in Table 2. It is clear that the total error of the analysis as well as that of both major components is markedly lower when using the plasmatron. The results also show that the effect of the composition of the sample is substantial when using the a.c. arc. When using the plasmatron the 'instrumental error' and the "sample error" are of the same order of magnitude.

The systematic errors in the analytical results obtained for each element were found to be negligible at the 5 % level of significance with 23 degrees of freedom when using the plasmatron.

Table 2. Results of variance analysis of elements in natural rock samples (relative %)

Element	σ_r		σ_c		σ^Σ		d	
	Plasmatron	ACA*	Plasmatron	ACA	Plasmatron	ACA	Plasmatron	ACA
Be	3.7	12.0	1.3	16.4	3.92	20.32	0.03	5.6
Co	5.1	10.3	3.2	17.8	6.02	20.57	−0.02	2.4
Cr	3.6	11.2	3.2	19.8	4.82	22.74	0.11	−1.8
Ga	2.8	12.4	1.8	16.4	3.3	20.54	0.05	6.0
Mn	4.3	13.5	1.3	18.6	4.49	22.98	0.20	3.2
Mo	5.2	8.2	2.3	12.8	5.68	15.20	0.10	−2.3
Nb	2.5	8.5	2.8	19.3	3.76	21.10	−0.05	−1.8
Ni	3.7	9.5	2.6	19.2	4.53	21.42	0.11	6.2
Pb	3.2	16.0	4.5	15.0	5.52	21.93	0.22	2.8
Sc	6.4	14.1	3.5	18.5	7.29	23.26	0.15	−2.0
Sn	4.9	15.7	3.8	16.3	6.20	22.63	0.052	5.7
Ti	5.8	14.5	2.2	24.7	6.24	28.64	0.032	4.2
V	4.3	15.0	3.2	18.5	5.36	23.81	−0.10	4.2
Zr	5.2	9.4	1.5	16.4	5.41	18.89	0.42	7.4
La	3.5	10.3	3.5	14.8	4.95	18.06	0.10	−2.9
Y	3.8	12.8	2.2	16.3	4.39	20.74	0.02	3.8
Yb	4.2	9.8	1.4	15.9	4.43	18.35	0.11	7.2

*Alternating current arc.

[8] A. S. Cherevko, *Spectroscopy (Methods and Applications)*, p. 352. (Russ.). Nauka, Moscow (1969).

[9] P. W. J. M. Boumans, *Theory of Spectrochemical Excitation*. Hilger and Watts, London (1966).

[10] T. S. Melnikova and V. V. Pickalov, *Beitr. Plasma physik* **22**, (2) (1982).

[11] M. K. Asanaliev, Study of plama flow of two-jet plasmatron (Russ.). Thesis, Frunze (1979).

[12] K. Doerffel, Statistics in analytical chemistry, MJR, M (1969).

3.2. *The temperature distribution in the analytical region of the plasma*

The most important physical parameters of an excitation source are the temperature and the electron density since they determine the spectral nature of the plasma, i.e. they determine the intensities of line spectra, continuous background radiation and band spectra.

A three-dimensional temperature distribution in the region where the two plasma jets merge was obtained by installing the plasmatron so that a horizontal image of the plasma could be projected onto the slit of the spectrograph. By examining 4 cross-sections at 1, 7, 19 and 31 mm from the intersection of the two jets and using different observation angles at each distance it was possible to calculate local intensities in the plasma using the algorithm of the normalised Radon inversion. (A detailed description of this algorithm and its application to the problem of the spectral topography of a plasma is given in Ref. [10]. This method provides information about local intensities at almost any point in plasmas which are not symmetrical about their axis.)

The temperatures obtained when using pure graphite powder and graphite powder containing 25 % NaF were calculated from the intensities of the line pairs Zn I 307.2–307.6 nm and Zn I 307.2–328.2 nm. The equations and the relevant transition probabilities were obtained from Ref. [9].

Figure 5 shows an example of a cross-sectional temperature distribution for the third section of the plasma flow, i.e. at a distance of 19 mm from the merging point of the two jets, in two mutually perpendicular directions for the two test samples. The section of the plasma represents a deformed ellipse. From the obtained cross-sectional temperature distributions in each of the four sections, the axial temperature distribution shown in Fig. 6 was derived. This figure shows that the presence of easily ionised substances has little effect on the temperature of the plasma at distances of 25–30 mm from the merging of the jets but that at smaller distances the effect of reducing the temperature increases as the distance decreases.
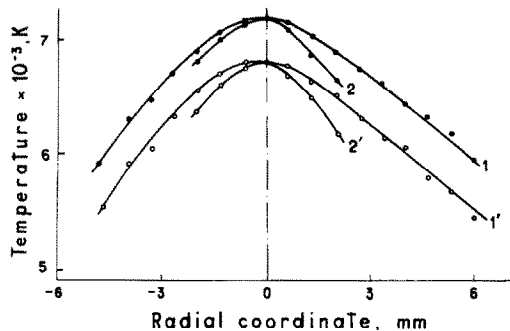

Fig. 5. Cross-sectional temperature distribution in the section located 19 nm from the intersection of the two jets. Curves 1, 1' and 2, 2' are for two mutually perpendicular directions, i.e. the axes of the approximately elliptic cross section. 1,2—without addition of Na; 1',2'—with addition of 25 % NaF.
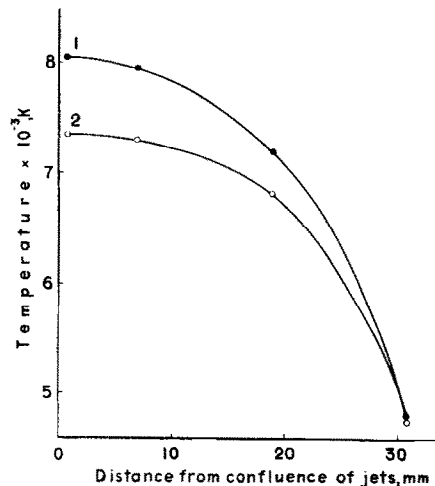

Fig. 6. Axial temperature distribution without (1) and with 25 % NaF additive (2).

4. Discussion

4.1. *Plasma temperature*

The dependence of the axial temperature distribution on the composition of the plasma is clearly associated with the distribution of the electric current density in the plasma. According to Asanaliev [11] the formation of a current in a plasma formed by the merging of two jets is the result of a semi self-maintained discharge, the current flowing in the region in the vicinity of the merging of the two jets. This current decreases with increasing distance from the point of merger the remoter regions being free of current. As anticipated, the temperature of these current-free regions is independent of the composition of substances introduced to the plasma.

Such a situation occurs in the two-jet plasmatron at distances greater than 30 mm below the point at which the two jets merge.

At distances less than 30 mm the presence of sodium has an increasing effect on the temperature such that a reduction of 700 K was observed for distances less than 5 mm. This value of 700 K is low when compared to reductions of 2000–4000 K in arc sources in the presence of alkali metals [13]. The relatively small decrease with the plasmatron implies that, where the semi self-maintained discharge exists, most of the heat supplied to these regions comes from radiation and conduction from the plasma jets, the contribution of resistive heating being small. This small dependence of the temperature of the plasma on the ionisation potential of the matrix components is one of the major reasons for the small effect of the matrix on line intensity and therefore on the analytical results.

4.2. *Electron density*

It is well known that the effect of easily ionised substances in the plasma is not restricted to temperature variations alone. Saturation of the plasma with vapours of low ionisation potential can lead to an appreciable increase in the electron density in the plasma and thereby can affect ionisation equilibria. That these effects occur in this source is clear since the curves in Fig. 3 show that the enhancing effect of sodium in the plasma is generally, but not in every case, greater the lower the ionisation potential of the element in regions far from where the plasma jets merge and where the effect of sodium on the temperature is relatively small.

4.3. *Mass transfer processes*

It should be noted that the ion line intensities in our experiments remained virtually unaffected by the addition of NaF, although they should have decreased as a result of both the temperature variation and a shift in ionisation equilibria. This suggests that the ions tend to accumulate at the axis of the plasma flow when sodium is present. Lack of data prevents us from further discussing the effect. So far we can only refer to the investigation of Schirrmeister [14], who noted that similar phenomena can be accounted for by means of variations in the internal radial electrical field resulting from ambipolar diffusion. Sodium weakens the field, as a result of which the diffusion of atoms and ions in the radial direction tends to be reduced.

In addition the increase in the electron density in the presence of sodium similarly reduces the ion transfer in the axial direction. The overall result therefore is a higher concentration of atoms and ions in the centre of the plasma than would occur in the absence of an easily ionised substance.

The enhancement effect of sodium in the current-free regions of the plasma may be explained by two factors:

(i) in the moving plasma the total concentration of the analyte elements and sodium decreases along the flow but the sodium is always present in significant amounts. Since the enhancement effect of sodium increases as the trace element concentration decreases there will be an enhancing of the line intensities of the trace elements along the flow of the plasma, and

(ii) this enhancement effect is not balanced by the effect of a temperature decrease, since the temperature is constant in regions remote from the merge of the jet.

[13] Ya. D. Raikhbaum and M. A. Luginova, *Zav. Lab.* **25**, 1449 (1959).
[14] H. Schirrmeister. *Spectrochim. Acta*, **24B**, 1 (1969).

The real situation is certainly more complicated but some of the reasons for the increase in line intensities caused by the interaction of the analyte substances and the plasma have been indicated.

5. CONCLUSION

The experiments have confirmed the superiority of the two-jet plasmatron as an excitation source over the a.c. arc for the analysis of samples with variable composition.

The insensitivity of the excitation conditions in the source to the matrix of the sample make it possible to select analytical conditions such that samples of different composition can be analysed using a single standard procedure and obtain relative standard deviations of the results of 4–6 % with detection limits in the range $10^{-5}–10^{-7}$ %. The high power used by the source makes it possible to analyse powdered samples directly provided the particle diameter is 5 μm or less.