

TUBE-ELECTRODE SPRAY METHOD IN THE EMISSION SPECTROSCOPY OF SOLUTIONS

By

E. GEGUS, E. KOCSIS and L. ERDEY

Research Institute for Iron Industry, Budapest and Department for General Chemistry of the Technical University, Budapest

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Introduction

The "classical" method of emission spectroscopy is the direct excitation of solid metal samples. The requirements of analysis, however, have early made the work with different samples important: a statistical study of the literature on emission spectroscopy for a longer period resulted in the following data for the distribution of papers [1]:

Analysis of solid metal samples:	23%
Analysis of powders	34%
Analysis of solutions	33%
Analysis of other samples	10%
	<hr/>
	100%

The statistical survey of papers on spectrographic analysis of solutions gave the following distribution of papers according to the way of introduction of samples into the light source [2]:

Flame excitation (flame photometric, spectrophotometric, spectrographic) spray methods	40%
Impregnated electrode method (spark or arc excitation)	25%
Solution residue technique	12%
Rotating disc method	10%
Porous cup method	7%
Other methods for solutions	6%
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	100%

The above table shows the spreading of flame excitation spray methods. Although the application of the method is limited by the relatively low temperature of the flame, the uniformity and easy control of sample introduc-

tion is advantageous. It seemed evident that a sensitive and generally applicable spectrographic method of good reproducibility could be obtained by combining the spray method with electric excitation of higher energy. This idea led to the developing of our tube-electrode spray method in 1953—54 [3], the theoretical study of spray and excitation conditions and practical applications of which are described below.

A survey of the literature shows that the development of emission spectroscopy of solutions ripened the method for the analysis of solutions which are continuously sprayed into the arc or spark.

We got to know only after elaborating our method that a tube-electrode spray method was suggested by MULD besides the rotating disc method for the analysis of silicate rocks and ores, by means of LUNDEGÅRDH's sprayer and spark excitation [4], but no other application of the method has been found so far. Experiments for spraying solutions into light sources have also been carried out by RUSANOV [5] by means of LUNDEGÅRDH's sprayer, and he has stated that the marked effect of composition and structure of solid samples during arc excitation can be eliminated by spraying the dissolved sample into the light source. It is interesting to mention that early experiments for simply combining the spray-method and spark excitation were carried out by RUSANOV [6] and LAMB [7]. A spray was introduced horizontally into the spark gap between two solid electrodes situated vertically, by means of a LUNDEGÅRDH type sprayer by EVANS and JOHNSTON [8]. They have also tried the tube-electrode method but found it disadvantageous because of salt deposits and the plugging up of the electrodes. An aerosol was introduced into the electrode gap between horizontally situated electrodes by means of Beckmann's sprayer by MALMSTADT and SCHOLZ [9].

Later on also other authors reported on the elaboration and application of various spray methods used in the emission spectroscopy of solutions. So, e.g. double revolving electrode method of GUTTMANN [10, 11] was also based on a pneumatic sprayer; GERKEN et al. [12] introduced an aerosol produced by ultrasonic sound into an A. C. arc between two horizontal electrodes from above; VOINOVITCH [13] sprayed solutions of bronze samples between horizontal electrodes; ZANAROLI and PIPPA [14] analysed lead ores by means of a sprayer similar to ours, but constructed independently of ours.

Since the above papers do not treat the theoretical aspects of tube-electrode spray method, they will not be dealt with here in detail. Only some papers of principal importance could be found in the literature that will be cited later.

A correlation can be found between the tube-electrode spray method and the plasma-jet method developed from the D. C. arc [15]. The excitation conditions are, however, so different from those of the above methods that it must be considered as a separate field.

Technical development of the method

The *pneumatic* spraying principle that has already been used since a long time in flame photometry, and is easiest to realize, was used to prepare an aerosol of the solution. Pneumatic atomizers can be divided into two groups: only the fine spray amounting to some per cent of the aerosol formed can pass the *indirect* (so called expansion chamber) atomizers, while a greater part of it flows back because of recombination. *Direct* atomizers use the whole of the formed aerosol. The most widely used type of atomizer in flame photometry is based on LUNDEGÅRDH's instrument [16], while GOUY's instrument described in 1879 [17] can be considered as the ancestor of the former. A generally

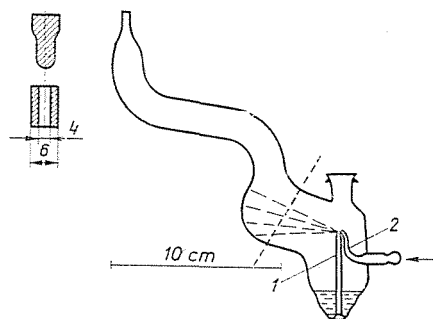


Fig. 1. EGK-I atomizer (EGK: initials of the authors' names). 1. Sucking capillary, 2. blowing capillary. Cutting the device along the dotted line it can be used as a direct atomizer

known representative of the type is the atomizer of RAUTERBERG—KNIPPENBERG [18] built into the Zeiss flame photometer. The best known type of direct atomizer modified for the purposes of flame spectrophotometers is Beckman's concentric injector, of which also an important Hungarian version exists [19].

For our purposes an instrument belonging to the group of the so-called indirect suction atomizers with an internal reservoir was chosen; a version of the type is shown in Fig. 1. The instrument was fixed to the optical bench by an adjustable holder. The most important point of view in the choice of the type was that the atomizer had to give fine aerosol to a suitable amount, to consume little solution (flow-back into the internal reservoir) to work at relatively low over-pressure, to be easy to produce, use and clean.

A version with a ground glass joint was constructed for the purposes of the theoretical investigation of the method (Fig. 2), in which capillaries of various size can be placed. Later on a version that could be fixed to a stand (Fig. 3) and another one ensuring larger surface and constant level of the solution, equipped with capillaries of different sizes (Fig. 4) were constructed*.

* We thank T. KÁNTOR for his help with the construction of the atomizers and also for his useful practical advice.

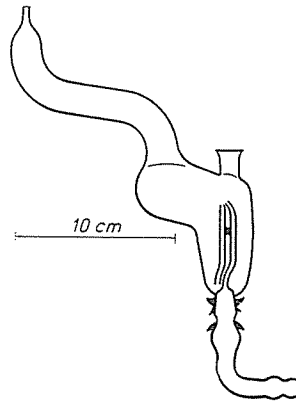


Fig. 2. EGK-II. atomizer, with interchangeable capillaries

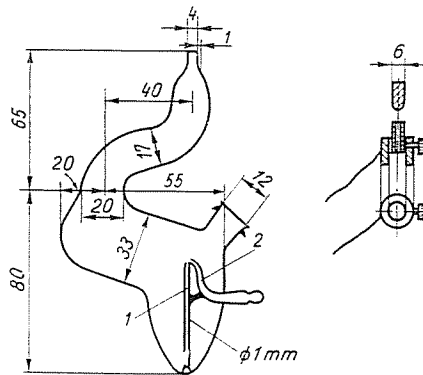


Fig. 3. EGK-Ko-I atomizer (Ko means a modification made by one of the authors)

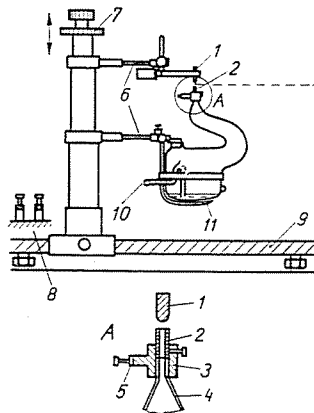


Fig. 4. EGK-Ko-II atomizer. Cross section of the electrode holder: 1,2. electrodes, 3. electrode clip, 4. end of atomizer, 5. electrical joint, 6. holders, 7. adjusting screws, 8. output of the source unit, 9. optical bench, 10. introduction of spraying gas, 11. holder of the atomizer

The results obtained by means of the above instruments [20] are summarized in the next chapter.

In order to improve the atomizer, and to determine the optimal size of capillary and test-conditions of spraying, several instruments having different

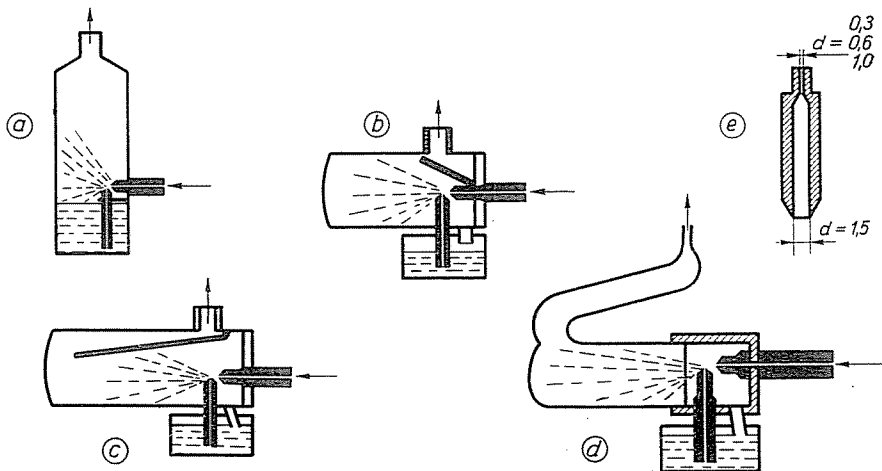


Fig. 5. Experimental atomizer types made of plastic material (types a-c plexi-glass), and combined with glass (d); with plastic material capillaries of different sizes (e)

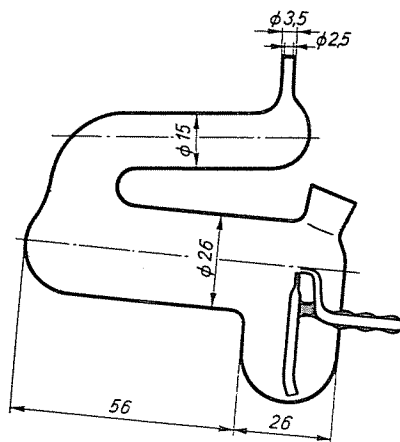


Fig. 6. EKG-G atomizer (G means a modification made by one of the authors)

arrangements were made of plexi-glass (Fig. 5). On the basis of these experiments described also in the next chapter, a small atomizer was constructed which was easily producible of glass and was easy to fix to the electrode stand (Fig. 6).

The aerosol was injected into the arc or spark discharge through a tube-electrode. The advantages of this as compared to the version spraying the aerosol between two solid electrodes will be given in the chapter dealing with

the conditions of excitation. In order to avoid corrosion caused by the acidic spray the graphite (and in some cases copper) electrodes were mounted on graphite pins [3], then they were more simply fixed with graphite-ended electrode clips [22]. In order to facilitate the adjustment to the optical axis, the

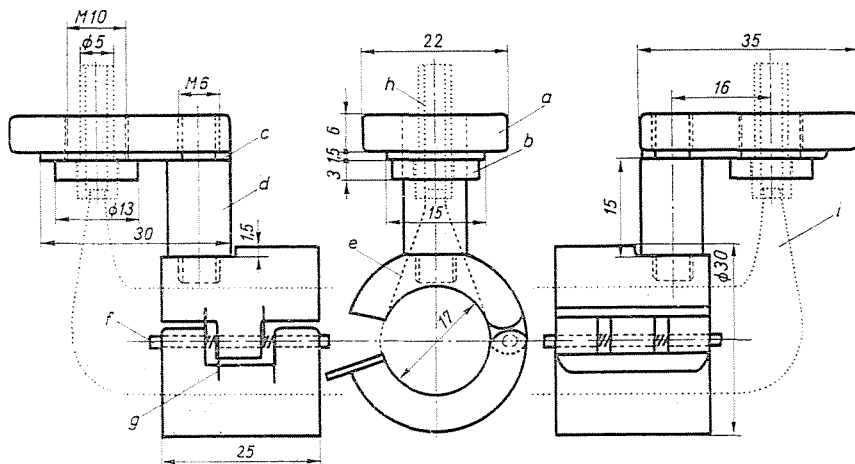


Fig. 7. Atomizer- and electrode holder for the EGK-G atomizer (a: teflon cover; b: graphite or copper (bronze) ring; c: brass plate; d: brass holder; e: holder made of plexi-glass; f: steel shaft; g: steel spring; h: tube-electrode; i: atomizer)

tube-electrode was enclosed in a copper ring that could be mounted to the atomizer and ensured electric joint (Fig. 4), then an electrode and atomizer holder with graphite or copper filling (Fig. 7). The holder is suitable for producing an atmosphere other than air if made from a teflon plate and silica tube [21].

Study of spraying conditions

A thorough theoretical study of the mechanism of spraying [20] has contributed to the determination of the optimal conditions of spraying. The following data were determined by means of theoretical calculations for pneumatic spraying: a) flow rates (v_{kr}) minimally necessary for drop division as function of drop size (r), surface tension of drop (σ) density (ρ_k) and kinematic viscosity (ν_k) of the medium (Fig. 8) from the following equation:

$$v_{kr} = 0,8 \sqrt[3]{\frac{\sigma^2}{10 r \rho_k^2 \nu_k}}$$

b) absolute (v) and relative ($c-v$) (to the gas = c) rate of drops in the aerosol within the atomizer that depend on their size, from the opening of the sucking

capillary to the inner deflecting wall from the following equation (Fig. 9):

$$v = c - \frac{1}{\frac{9,375^2 \gamma_k^2 v_k t^2}{\gamma^2 d^3} + \frac{18,75 \gamma_k v_k^{0,5}}{\gamma c^{0,5} d^{1,5}} t + \frac{1}{c}}$$

where

- γ_k is the specific weight of blow gas
- γ is the specific weight of the drop
- d is the diameter of the drop

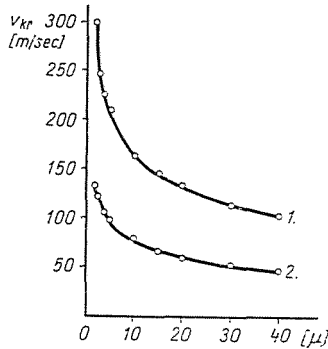


Fig. 8. Flow rates minimally necessary to drop distribution as function of the diameter of drops. (1: water; 2: n-propyl-alcohol)

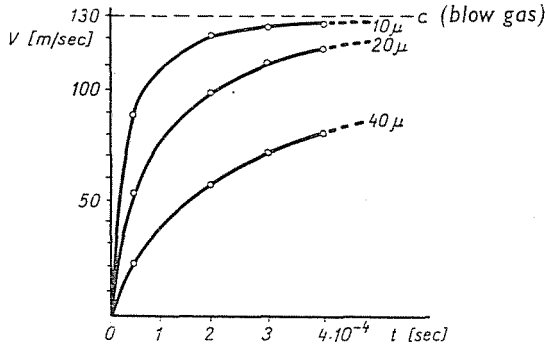


Fig. 9. Absolute and relative rates of the drops of aerosol of different diameters, as function of time, for flow-rate of blow gas $c = 130$ m/sec

c) path length of drops inside the atomizer, under the given experimental conditions (Fig. 10):

$$s = \int_0^t v dt$$

The comparison of the above data showed that — in contradiction to calculations of LANE [23] — droplets even smaller than 5μ could be formed in pneumatic atomizers, and not only from solutions containing detergents, but also from aqueous solutions without any detergent. In order to prove this, we caught the drops on a sooty plate and subsequent counting under microscope

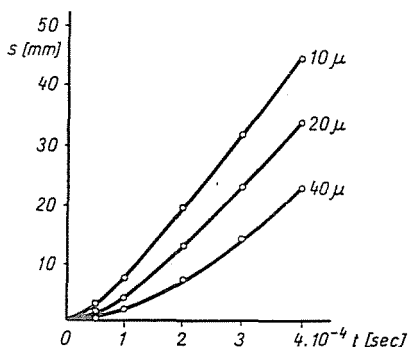


Fig. 10. Path length of the drops of different diameter inside the atomizer, as function of time

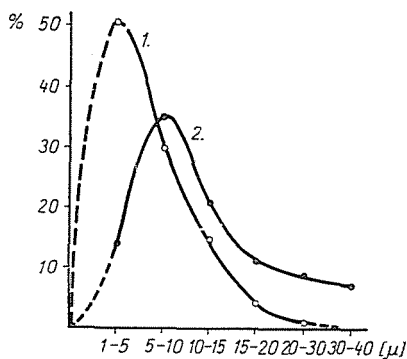


Fig. 11. Drop size distribution for alcohol (1) and water (2)

showed that the average size of drops leaving the EGK type indirect atomizers is around 5μ (Fig. 11). Fig. 12 demonstrates the size-distribution of drops produced in the direct (Fig. 1) and in the indirect atomizer. The following statements are based on our further experimental results [20, 21].

The efficiency of our atomizers, i.e. the amount of the secondary spray in the per cent of the primary spray is generally between 3–6%.

In flame photometry the fineness of aerosol leaving the atomizer is of primary importance. In spectrography, however, the amount of spray getting into the electrode gap is more important. The recombination of drops in the atomizer is less if the aerosol is finer, thus the efficiency will be higher.

The spray can be made finer by using a tight capillary, but a greater pressure is necessary to produce the same amount of spray during unit times that is to reach the same "spraying rate". It is not advisable to use very tight capillary because of the danger of plugging up.

Although the amount of spray can be influenced by the variation of diameter of the blowing capillary, first of all the diameter of the latter controls

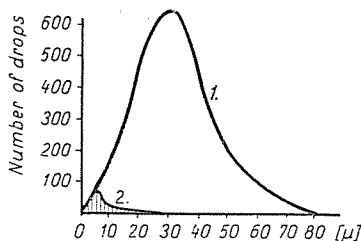


Fig. 12. Drop-size distribution curves for EGK type atomizer, for the case of water. 1. direct version (primary spray), 2. indirect version (secondary spray)

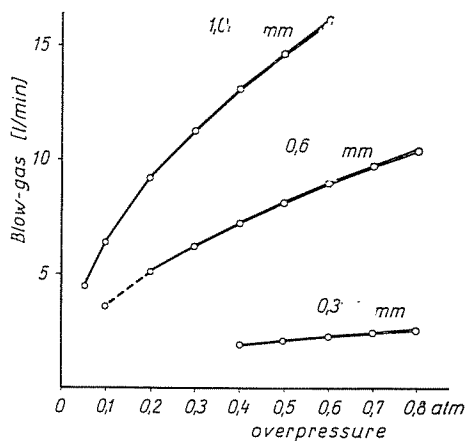


Fig. 13. Influence of the diameter of the outlet of blowing capillary on the relationship between the pressure of spraying gas and amount of gas passing through the instrument. (The breadth of the line gives information on the amount of spray.)

the relationship between the pressure and flow rate of gas (Fig. 13). It is disadvantageous to increase the flow rate of gas too much in emission spectroscopy because it decreases the intensity of the spectrum of the dissolved substance and increases that of the spectrum of the surroundings (atmosphere and electrodes). (This statement will be proved in the part dealing with excitation conditions.)

The dispersity of the aerosol increases with increasing pressure of spraying gas, but also the flow rate is higher.

The flow rates of secondary spray and spraying gas are also affected by the diameter of the outlet tube of the atomizer. So, for instance, increasing the diameter from 0.65 mm to 3.6 mm, an about 10% increase in $\log I$ can be observed, thus it is advisable to use a diameter as big as possible (2–4 mm).

In order to ensure constant speed of spraying it is important to keep the level of solution in the atomizer constant.

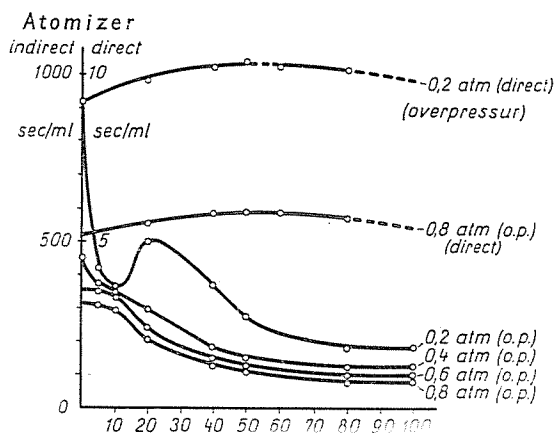


Fig. 14. Rate of spraying in the direct and indirect version of the EGK-I atomizer as function of concentration of propyl-alcohol, at different pressures

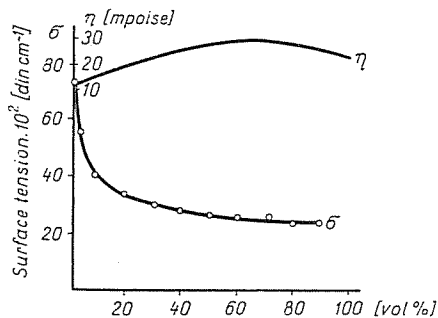


Fig. 15. Surface tension and viscosity of water-propyl-alcohol, plotted against the concentration of propyl-alcohol

The division of the drops can be made easier by reducing the surface tension. Thus for instance, making the spray finer by adding alcohol to the solution, in certain cases even a 30 per cent increase in the emission intensity could be observed [20]. This increase, however, cannot be unambiguously explained by the reduction in surface tension since no increase could be observed after addition of other detergents (synthetic detergents), even if they reduce surface tension [24]. It can be assumed that a polar

solvent accelerates the evaporation of the drops in the aerosol of aqueous solutions, so increasing the intensity of radiation, and also increasing the efficiency of the atomizer by producing smaller drops.

In fact the viscosity of the sprayed solution only influences the operation of the direct atomizer, while the efficiency of our indirect atomizer depends rather on the surface tension, as is obvious after comparing the curves in Figs 14 and 15.

The cooling observed at the beginning of spraying can be as great as some degrees; however, during the 1/2 minute pre-sparking before recording the spectrum an equilibrium sets in, so this cooling does not markedly affect the spraying conditions.

On the basis of the above said, the most important of factors influencing the conditions of spraying are the sizes of spraying capillaries, and generally, those of the atomizer. Since no instruments of precise sizes can be produced by glass technology, we have had different experimental types of atomizer made of plexi-glass (Fig. 5). On the basis of studying them [21] we have found, however, that no efficient indirect atomizer that could meet the requirements can be produced of plastic materials because of the strong recombination of drops on their surface. As for the shape of the device, care should be taken that the spray must not be opposed to the gas stream, and no turbulence should be formed, as in types 5a—c. Only the top of atomizer 5d was made of plexi-glass, while the chamber and tubing was made of glass. The use of plexiglass spraying capillaries of well defined sizes (5e) made the investigation of the relationships possible between the conditions of spraying by means of the instrument. By taking the glass portion off, the device can also be used as a direct atomizer. The experimental atomizer was produced with an external reservoir, the final version (Fig. 6), however, had an internal reservoir, thus avoiding the leaking of acid fumes under the device.

On the basis of the above said the *optimal parameters* of our device are as follows:

Diameter of the outlet end of blowing capillary	0.6—0.7 mm
Diameter of the outlet end of sucking capillary	0.3—0.4 mm
Diameter of the outlet end of spray chamber tube	2—4 mm
Overpressure of gas	0.3—0.6 atm
Flow rate of gas	6—10 l/min
Rate of spraying (solution consumption)	0.1—0.2 ml/min.

It is most important to adjust first of all the rate of spraying if other parameters are in the above intervals, on the basis of the real solution consumption measured [21] and properties of the solution (nature, concentration of the solute etc.). The amount of spray must be adjusted by the pressure so that enough solution could be supplied to the upper electrode, but no deposit of salt could be formed. If the parameters of spraying of various devices are known, not only the operation of one atomizer can be suitably adjusted but the devices can even substitute one another, and routine analyses can be carried out by choosing a suitable series of devices, pouring the solutions into the atomizers previously and changing the atomizers (e.g. routine analyses by spectrometers).

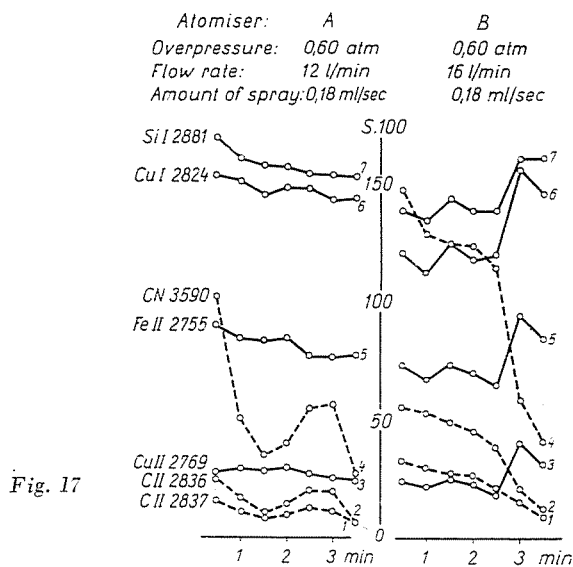
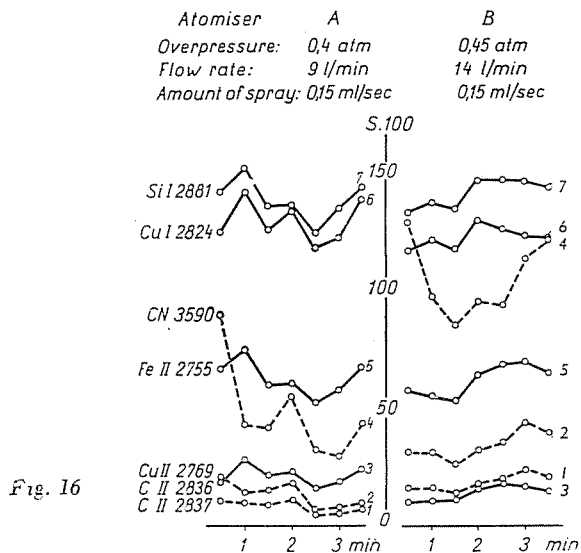
The small differences between the various atomizers may not influence the results of analyses, or the reproducibility of measurements carried out in different laboratories, since an internal standard is used during the analyses.

Investigation of excitation conditions

It is a great advantage of spectrographic methods using solutions as compared to those using solid samples that no inhomogenities exist in the solution, and solutions can contain the reference element also in homogeneous distribution. The components of solution sprayed into the arc or spark may, however, behave differently: fractional evaporation, diffusion, various reactions can take place between the substance to be investigated and its surroundings, on the electrodes or in the plasma. The danger of fractionation into elements is much less for techniques using continuous sample introduction than for discontinuous techniques. The continually reformed solution surface produced in our tube-electrode method by means of spraying at a suitable rate practically eliminates the danger of fractionation [3], as proved by dispersion (stand. dev.) investigations and "sparking off" curves obtained by a series of measurements with different solutions [25] and by recordings produced by a photoelectric adapter [26].

In this context the influence of the most important factors: rate of spraying, pressure and gas flow rate on the sparking effect was studied [21].

According to Figs 16 and 17, too high gas flow rate makes the lines of carbon electrodes and the cyanogen bands stronger (B atomizer), as was already mentioned in connection with the spraying conditions. If the rate of spraying is reduced, the line intensities in time decrease below a given limit, the lines of the electrodes and the cyanogen bands become more intense, and obviously the solution supply will be small and the plasma becomes deficient in the substance to be investigated.



Figs. 16 and 17. "Sparking-off" curves on the basis of a series of spark spectra, taken by a Zeiss PGS 2 grating spectrograph, with continuous spraying of solution of a mineral sample (W-1 standard) ($C = 12 \text{ nF}$; $L = 0,3 \text{ mH}$), in the case of different parameters of spraying

ZHURAVLEV and NEMCEVA [27] have reported similar experiences; they have stated that aerosols containing solutions of metal salts stabilize spark discharges, while they make the spectrum of copper electrode weaker.

As for the *mechanism of excitation*, we have stated on the basis of our first experiments, that the thin, continually re-forming solution layer on the upper

electrode placed in the way of the aerosol plays an important role in the evaporation and emission of the substance to be studied. Control experiments were carried out with aerosol sprayed in perpendicularly between solid electrodes — similarly to the method of EVANS and JOHNSTON [8], and the sensitivity was found to be one order of magnitude lower than that of the tube-electrode method.

In order to determine the axial distribution of excitation, the spectrum of the solution of a mineral sample (W-1 standard) focused on the whole length of the slit and photographed by a Zeiss PGS 2 grating-spectrograph was studied under different excitation conditions [21].

Comparison of Figs 18 and 19 shows that in the spark of high energy ($L=0,02$ mH) nearly homogeneous emission distribution can be found along the axis of the electrode gap, the spectrum of the electrodes is also intensive, the energy of the plasma is satisfactory to the direct excitation of the aerosol; while in a spark of low energy and long time constant ($L = 5$ mH) the sample is excited mostly in the vicinity of the upper electrode; the spectrum of the electrodes can be observed only in the close vicinity of the lower tube-electrode. Sparks of medium energy (Fig. 20) — according to our general experiences — are the most suitable for the simultaneous determination of various elements present in the sample, since in such a case the intensity distribution is still satisfactory, and the spectrum of the electrodes is not predominating. Under the same conditions but at lower rate of spraying (Fig. 21) the spectrum of the solution becomes weaker, while that of the electrodes more intense, in concordance with our experiences demonstrated in Figs 16 and 17. The above said are in agreement with the observations of PAKSY on separation or overlapping or vapour spaces in discharges of different energies [28].

During the investigation of the excitation conditions experiments were also carried out in atmospheres other than air [25]. It has been stated that reactions taking place in the plasma of the light source have a marked effect on the radiation of various elements (e.g. oxidation for Al). Argon atmosphere which hinders chemical reactions is often advantageous in emission spectroscopy, but, because of its remarkable background intensifying effect in the tube-electrode spray method, it was not found to be particularly advantageous.

Nevertheless, on the basis of the analogy of plasma jet method and new experiments of PAKSY [29] special advantages of the use of argon atmosphere can also be expected.

Interelemental effects

Fractionation mentioned above in connection with excitation conditions can be accounted for here. According to KULCSÁR [30] there is really no fractional evaporation in the tube-electrode spray method, but the difference

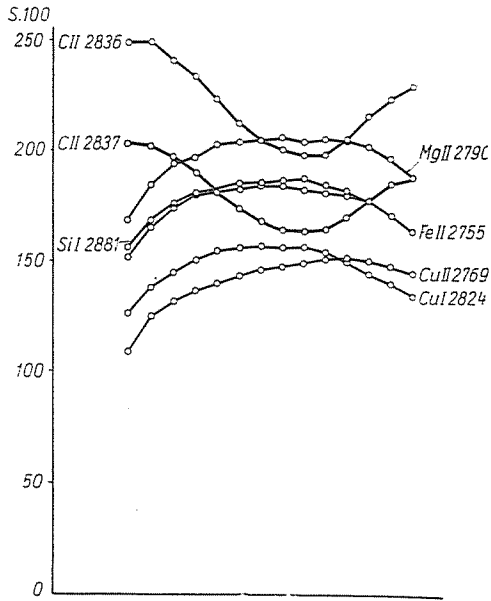


Fig. 18

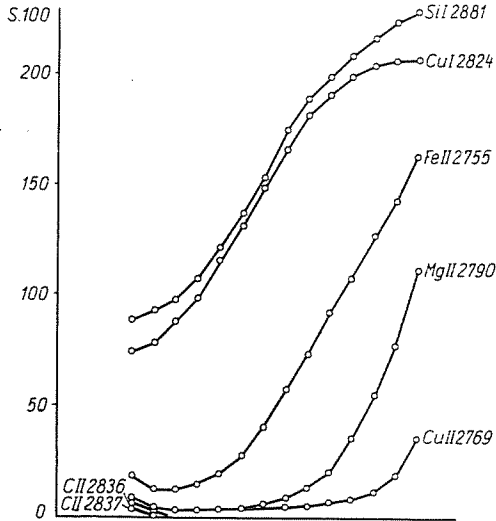


Fig. 19

Figs 18. and 19. Emission distribution along the axis of the spark gap. Lower electrode on the left, upper electrode on the right

For Fig. 18: $C = 12 \text{ nF}$; $L = 0,02 \text{ mH}$; $p = 0,40 \text{ atm}$ (overpressure)

For Fig. 19.: $C = 12 \text{ nF}$; $L = 5 \text{ mH}$; $p = 0,40 \text{ atm}$. (overpressure)

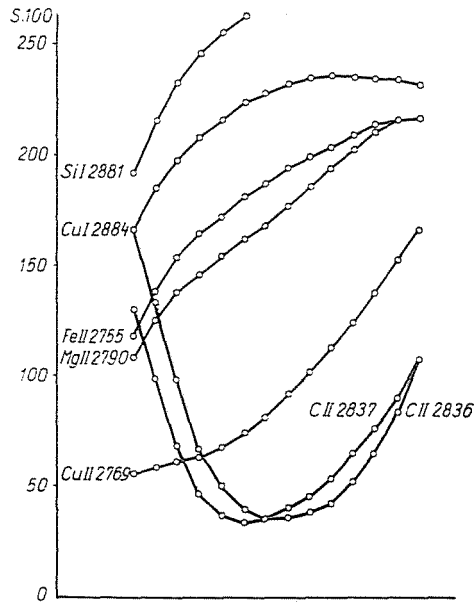


Fig. 20

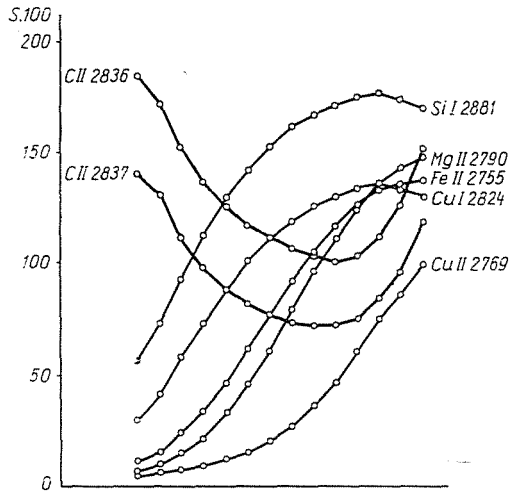


Fig. 21

Figs. 20 and 21. Emission distribution along the axis of the spark gap. Lower electrode on the left, upper electrode on the right.

For Fig. 20: $C = 12$ nF; $L = 0,3$ mH; $p = 0,40$ atm (overpressure)

For Fig. 21: $C = 12$ nF; $L = 0,3$ mH; $p = 0,20$ atm (overpressure)

between the ionization potentials for different elements causes a so-called "third element effect".

In the mentioned paper ZHURAVLEV and NEMCEVA [27] have also stated that elements of low ionization potential have the greatest weakening effect on the spectrum of the electrodes, but they could not find an unambiguous relationship between the observed effects and ionization potentials.

After surveying interelemental effects in connection with the study of nonconducting materials [31] we have stated that in our case no interelemental effect could be observed because of the buffering effect of alkali metal (Na) present in a great amount, and because of the matrix-effect of internal standard element (Co or Cu) of high ionization potential, only a little increase of standard deviation can be found during the determination of some components.

In the analysis of metals and alloys (aluminium, iron, steel, nickel, cobalt) the matrix effect is predominating in the absence of alkali metals, and it is superfluous to add an alkali buffer, for it causes an intensification of background in the spectrum.

The anion effect is optimal — in concordance with the observations of KULCSÁR — in 1 + 4 hydrochloric acid.

The situation is critical from the point of view of interelemental effects only if elements of extreme properties (very high melting point; incorporation into the electrode — e.g. Zr) are in question. In such cases the sparking effect of solutions and the precision (standard deviation) of the determination can become anomal.

Sensitivity and reproducibility of the method

The sensitivity of methods using solutions are — according to the investigations of SCHLISSMANN [32] — in many cases not lower than that of those using solid samples. According to our comparison studies [33] the tube-electrode method generally ensures higher selectivity than other methods using solutions, because of its better reproducibility and because of the suppression of the mentioned interfering effects. Naturally, the appropriate adjusting of spraying and excitation conditions are very important.

With methods producing continually re-formed solution surfaces the sensitivity is affected first of all by the thickness of the solution layer. According to the experiments of NEDLER and EFENDIEV with fulgurator [34] the sensitivity remarkably increases with decreasing layer thickness. The experiments of RUSANOV and SOSNOVSKAYA with rotating disc electrodes [35] have also proved that the sensitivity is higher for thinner solution layers, but also fractional evaporation can be observed, while with thicker layers the sensitivity is lower, but the reproducibility increases. These data have led us nearer to the

improvement of sensitivity and reproducibility, and to the finding of the optimal conditions for analysis.

The reproducibility and sensitivity were determined for various analytical applications of the tube-electrode spray method in concordance with the definition of our cited paper [33].

Also the absolute sensitivities will be given for the determinations listed below.

Practical applications of the tube-electrode spray method

Determination of germanium in solutions

Determination of arsenic in lead [3]

In the first example the application of our method Ge content of solutions was determined with Sb internal standard element to an absolute sensitivity of 10^{-6} g. Also the OH band head could satisfactorily be used as reference.

Arsenic content in lead can be determined even beside great amounts of Sb by means of standard solution samples that can easily be produced.

Determination of Mg, Zn, V, Cr in aluminium [36]

Synthetic solution standard samples and fixed calibration curves were used, with a background correction. The reproducibility and sensitivity of the determinations were found to be better than those for the solution residue technique. The sensitivity of V determination was increased by an enrichment with extraction. Sensitivity of the method (without enrichment):

Element	Lower limit of determination	
	relative %	absolute, 10^{-6} g
Mg	0.001	0.1
Zn	0.008	1.4
V	0.003	0.5
Cr	0.003	0.3

Determination of gold in ores and concentrates [37]

0.5 g/t can be determined in 5 g of sample by enrichment on a metallic tellurium collector, with Te or Pt internal standard element. This corresponds to an absolute sensitivity of $5 \cdot 10^{-7}$ g Au.

Determination of V and Ni in oils [38]

Mineral oil and residual oil can be introduced into the spark gap after dilution. Cobalt-oxinate was used as internal standard added to the diluted oil as a solution in chloroform. The sensitivity of the method is 1–5 ppm for V, and 5–20 ppm for Ni, according to the type of oil.

Analysis of slags [39]

Chemical composition of blast furnace and open hearth steel-making slags was determined in a hydrochloric acid solution obtained after a fusion with NaOH in a silver vessel, using Co or Cu internal standard. The complete analysis only required 40 minutes, including the determination of SiO_2 , FeO, Cr_2O_3 , MgO, MnO, Al_2O_3 and CaO, in the usual concentration ranges for the components.

Analysis of inclusions, ores and other nonconductive substances [40, 41, 42, 52].

The method for the analysis of slags was extended to the analysis of various nonconductive substances (silicates, ores, isolated inclusions in steels, sand, silica bricks, magnesite, oil ash), after determining the suitable conditions for fusion, recording of spectra and evaluation. Also the TiO_2 and BaSO_4 content was determined besides the components of slags. Isolated inclusions of alloyed steels were analysed by means of a high-dispersion grating spectrograph (PGS 2) [21].

Experiments were made to compare [41] the tube-electrode spray method, the rotating disc method and the solution residue method. We have stated that the second and third method requires about 2.5 fold of the time required by the tube-electrode spray method, if the same accuracy is to be assured.

Analysis of coal ashes [43]

A tube-electrode spray method, using Co or Cu as internal standard elements was introduced for the determination of major components in silicates and coal ashes (SiO_2 , Al_2O_3 , Fe_2O_3 , CaO, MgO) in the Research Institute for Electrical Energy Industry and in the Chemistry Department of the Research Institute for Mining, on the basis of our earlier results. The method is used at present for routine analyses.

Determination of macro and micro elements in soil extracts [44]

The determination of Ca, Mg, Al, Fe, Mn, Cu in soil extracts was elaborated in the Institute for Agricultural Chemistry in Poznan by means of our method for the analysis of solutions.

Determination of acid-soluble SiO_2 content in concretes [45]

A method has been elaborated with our contribution in the Control Laboratories for Building Industry for the determination of SiO_2 (soluble in dilute hydrochloric acid) in concretes with the purpose of determining their cement content.

Determination of the components of glasses [46]

A tube-electrode spray method has been developed in the Central Research Institute for Building Industry for the routine determination of Ca, Mg, Ba and Al in technical glasses, in a hydrochloric acid solution obtained after fusion with KOH, by means of copper electrode.

Determination of Cr in blood and urine [47]

A tube-electrode spray method was developed in the Research Laboratories for Medical Service of the Hungarian State Railways for the determination of Cr content in blood and urine, after decomposition. The evaluation was made without the use of an internal standard on the basis of absolute densities obtained by Seidel's transformation (W). Cr contents greater than 0.01 ppm were determined from 10 g blood or 50 g urine.

Determination of trace elements in iron and steel

I. Cr, Ti, V [48]; II. Ni, Mo, Mn, Mg and Cu [49]; after enrichment Al, Pb, As, Bi, Ag and Zr [50, 53]. The metals mentioned below were determined in cast iron and plain-carbon steels, in their hydrochloric acid solution without any separation.

Element	Lower limit of determination	
	relative, %	absolute, 10^{-6} g
Cr	0.02	0.2
Ti	0.003	0.03
V	0.02	0.2
Ni	0.02	0.2
Mo	0.01	0.1
Cu	0.01	0.1
Mn	0.003	0.03
Mg	0.001	0.01

After separation and enrichment by solvent extraction, the following elements were determined using In or Be as internal standard element (Zr was also determined after separation with mercury cathode, using Ag as internal standard element).

Element	Lower limit of determination	
	relative, %	absolute, 10^{-6} g
Al	0.001	0.2
Pb	0.001	0.5
As	0.002	0.4
Bi	0.001	0.2
Ag	0.0001	0.02
Zr	0.003	0.2

Determination of trace elements in nickel

Under conditions similar to those in the above iron-analyses the following trace contaminants were determined by our solution-method.

Element	Lower limit of determination	
	relative, %	absolute, 10^{-6} g
Co	0.008	0.6
Fe	0.008	0.6
Cu	0.005	0.4
Mn	0.008	0.6
Si	0.008	0.6

Other applications

The tube-electrode spray method has been used for quite a long time at the Research Institute for Metal Industry for the determination of Mg and Fe in Mg—Al alloys, for the determination of Al, Fe, Si, Mg, Ti in bauxite, for the

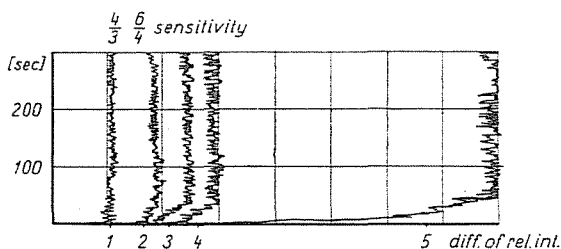


Fig. 22. Variation of the intensity of the line pair: V II 3110,7 — Fe I 4045,8 in the time, for solution samples of different V content; 1: 0,01%; 2: 0,05%; 3: 0,08%; 4: 0,10%; 5: 0,30% [51]

determination of the composition of coal ashes using Co as internal standard element, and also for the determination of trace contaminants in gallium metal (99.9%).

Spectrometric analysis of steels in solution

We have already referred to experiments carried out by means of a photoelectric adapter [26] in connection with sparking off uniformity of spraying which have proved that the method is also good for photoelectric recording.

A method has also been developed under our direction at the Laboratories of W. P. Rolling-Stock and Machine Works, Győr for the determination of 0.01—0.3% V and Mo content in steels, in form of solutions, by means of a Cameca Spectro-lecteur automatique instrument, with an EGK—Ko—I type atomizer [51]. According to Fig 22. the deflection of the recorder is proportional to the concentration, and the sparking effect is uniform. The above mentioned laboratories wish to spectrometric methods for the analysis of metals after dissolution use in the future. These analyses cannot be carried out in the solid state because of the lack of standard samples.

Collaborating with the Spectrographic Laboratories of Lenin Metallurgic Works in Miskolc experiments are being done in our laboratories in order to develop spectrometric applications of our method worked out for solutions, on an ARL—PC Quantometer. We are convinced that many difficulties emerging in the analysis of solid samples — effects of texture, inhomogeneities, surfacial effects etc. — and also problems arising during the analysis of high alloy steels, special alloys — such as the problem of standards — will be eliminated by preparing solutions of these and spraying the solutions into the light source. Further work is being done in order to resolve the above problems, and also to improve our method for the analysis of solutions.

Summary

The paper reports on results attained by a tube-electrode method that is generally applicable in the emission spectroscopy of solutions. The technical development and the optimal parameters for the operation of atomizers and also the optimal conditions of spraying are treated in detail. The validity of empirical relationships known between the size of drops produced in pneumatic atomizers, the rate of the spraying medium, the viscosity and surface tension of the solution have been proved by theoretical calculations. Statements were made as regards the mechanism of excitation and axial distribution of the emission. Interelemental effects, the sensitivity and reproducibility of the method are also treated. Some practical applications of the method are also given.

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Prof. Dr. László ERDEY, Budapest, I. Fenyő u. 11.

Ernő GEGUS, Budapest, II. Lupény u. 12.

Dr. Elemér KOCSIS, Budapest, VIII. Delej u. 28.