

[54] **DEVICE FOR SPECTROCHEMICAL ANALYSIS OF SOLUTIONS**

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[58] Field of Search **356/36, 85, 86, 87**

[56] **References Cited****UNITED STATES PATENTS**

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[57]

ABSTRACT

A device for the quantitative spectrochemical analysis of solutions uses two spark discharge electrodes. One of the electrodes is a carbon rod electrode whose one end is shaped as a truncated cone and has a semi-spherical end surface. The other electrode is a circular carbon disc electrode which has a rotary drive and is located beneath the rod electrode. A condensing chamber atomizer is provided for producing a flow of aerosol from the solution to be tested and a jet for the flow of aerosol is directed at the disk outside the spark discharge zone. The device uses optical and electrical equipment comprises among other things a lenticulated condensor, multichannel spectrometer and photomultipliers.

4 Claims, 8 Drawing Figures

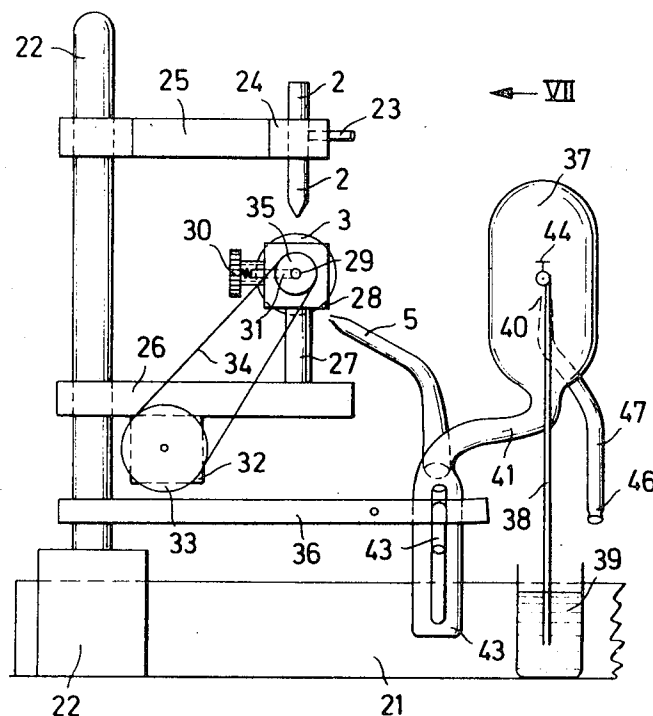


Fig. 1

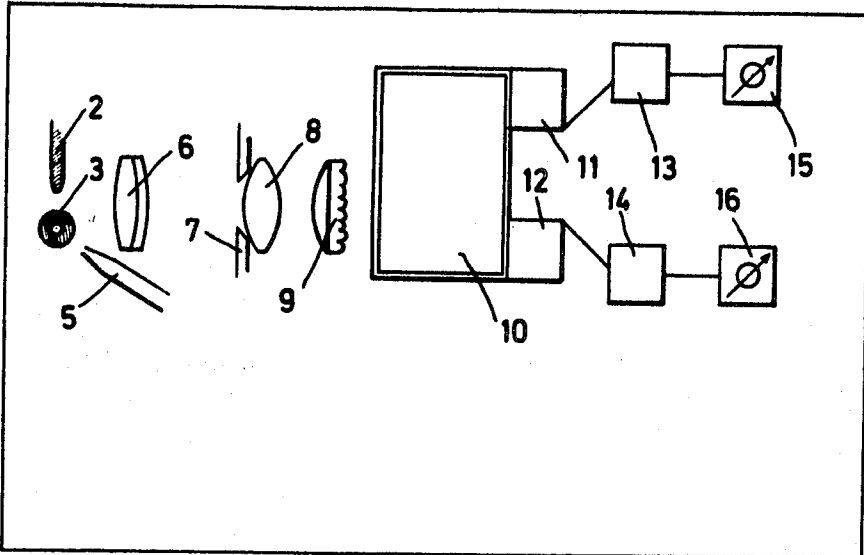
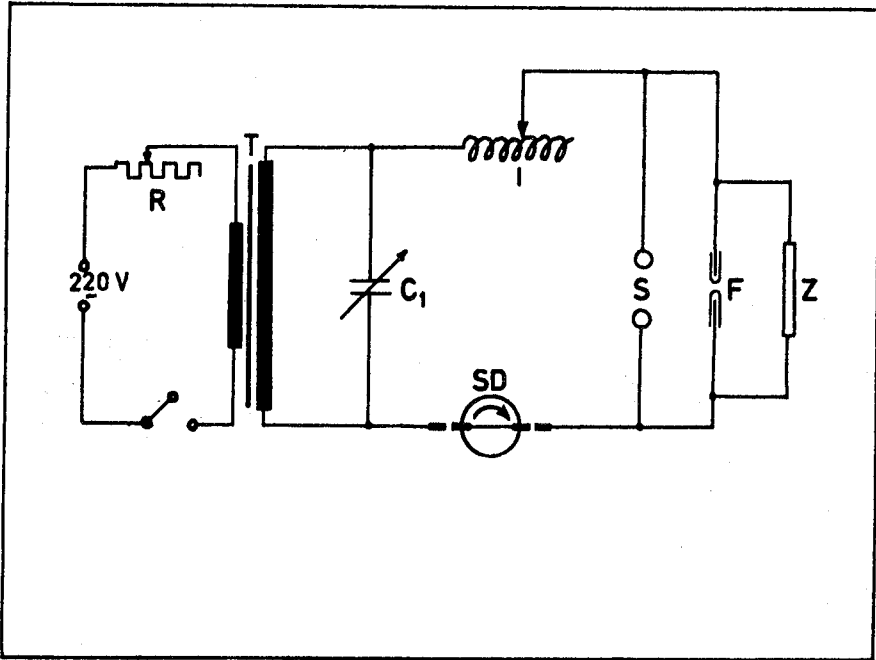


Fig. 2



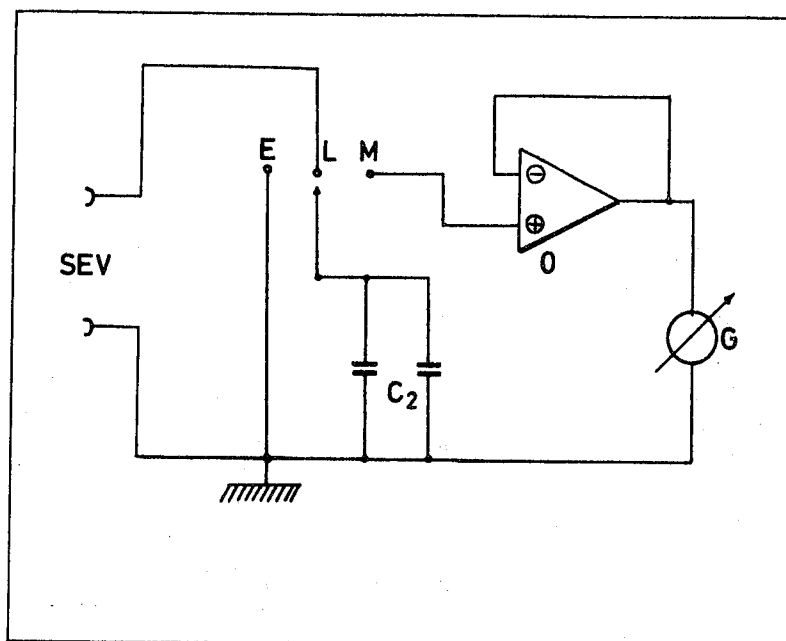


Fig. 3

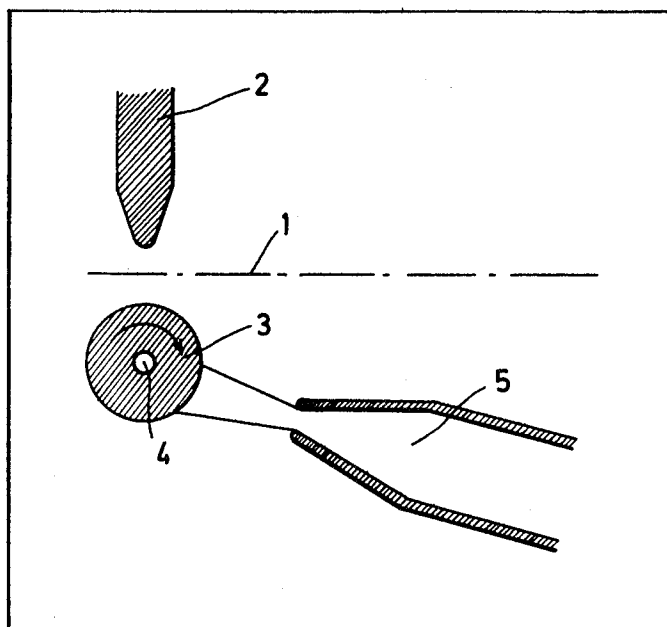


Fig. 4

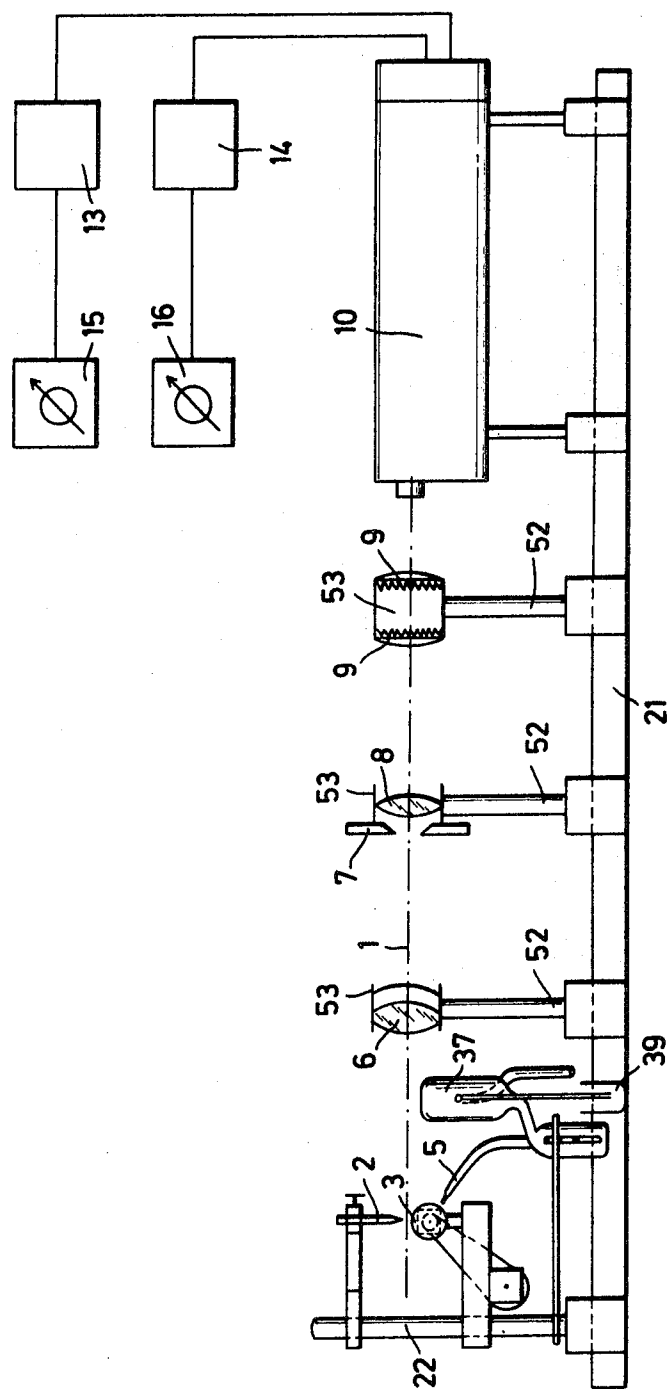


Fig. 5

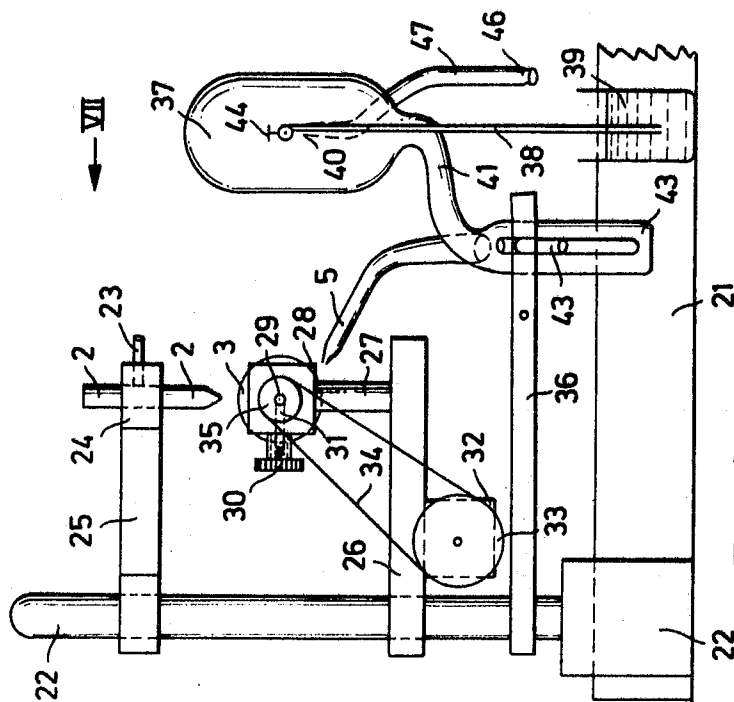


Fig. 6

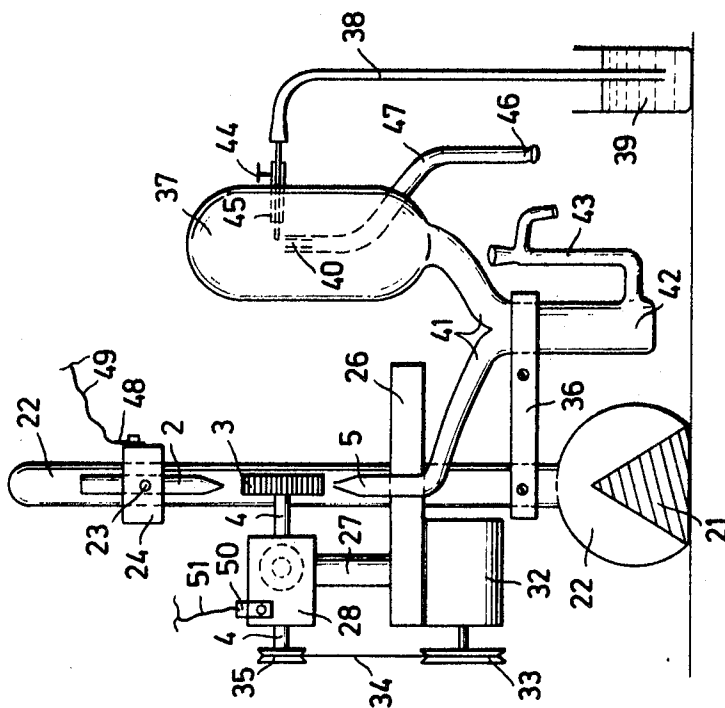


Fig. 7

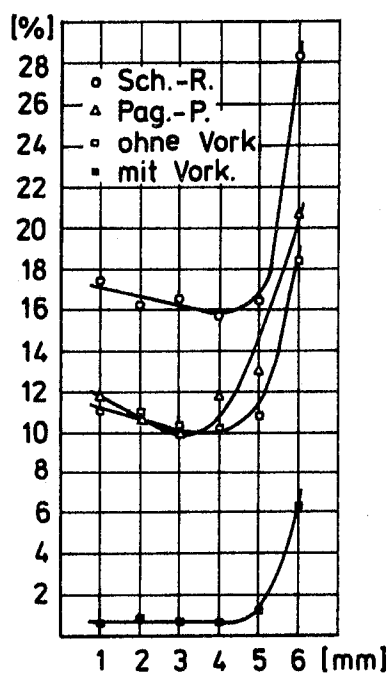


Fig. 8

DEVICE FOR SPECTROCHEMICAL ANALYSIS OF SOLUTIONS

BACKGROUND OF THE INVENTION

1. Field to Which Invention Relates

The invention relates to a device for the quantitative spectrochemical analysis of solutions using two spark discharge electrodes one of which is a disk having a rotary drive, and means for applying the solution to the periphery of the disk.

2. The Prior Art

In addition to such a device employed by Pagliassotti and Porsche, a variety of other devices for quantitative spectrochemical analysis of solutions has been proposed in the past few decades. Although it was the dissatisfaction with the accuracy of the obtainable results that caused the development of the relatively large number of processes known today the problem was however not solved satisfactorily by any of these proposals.

In the beginning, attempts were made to vaporize and excite the solution, which was filled into carbon or metal cups, by sparking with a counter electrode (crater electrode, disk electrode according to Gerlach, sparking tube according to Twyman and Hitchen). These procedures, however, lead to semiquantitative results at best. Later on, Scheibe and Rivas applied small measured amounts of a solution to be tested and analyzed to the surface-ground ends of cylindrical auxiliary electrodes made of carbon for spectroscopic use and dried them by warming them up. Through sparking the end surfaces, the specimen were vaporized and excited. More recent processes were introduced by Feldmann, who permits the solution to drain through a porous cup electrode into the path of the spark, and also by Pagliassotti and Porsche who apply the solution by submerging and rotating the above mentioned disk electrode in the specimen, as well as by Zink, who suggests using vacuum cup electrodes which utilize the spark-discharge itself for atomizing the solution.

It has also been tried to introduce atomizer-produced aerosols into the discharge gap through perforated auxiliary electrodes or by spraying them directly at rigidly mounted auxiliary electrodes. Although flame spectrometry, in which the solution to be analyzed is similarly sprayed into a flame as the aerosol, indicates with great accuracy the elements excitable at flame temperature, these efforts have not produced hitherto results with the desired accuracy.

It is an object of this invention to increase the accuracy of quantitative spectro-chemical analyses of solutions.

SUMMARY OF THE INVENTION

The invention is based on the realization that in the above mentioned methods known to date the aerosol cannot enter the discharge region in predetermined and reproducible amounts, which is caused by a thermal expansion of gases present moreover, because of a consequently disrupted spark discharge, the required amount of aerosol cannot be enforced by the application of a higher spray pressure. To overcome this disadvantage, this invention proposes a device of the above mentioned category, but improved and provided with an atomizer to produce a flow of aerosol from the solution, and a jet for the flow of aerosol directed at the disk outside of the region of spark transition.

The aerosol can be applied to said disk totally unhindered while it is steadily being rotated, and the aerosol reaches the region of spark discharge dried and in exactly required and reproducible amounts. In this way results of analysis can be obtained with a resultant inaccuracy and deviation amounting to approximately only one-tenth of those possible so far.

In order to obtain an aerosol with the smallest possible droplets, the most practical atomizer to use is a condensing chamber atomizer in whose condensing chamber the larger droplets are arrested and deposited. The atomizer could also be an ultrasonic atomizer or an electrostatic atomizer.

According to a preferred embodiment of the invention the jet should be directed — as seen in the direction of rotation of the disk — toward the second quarter of the disk periphery located behind the region of the spark discharge.

As an embodiment of the invention the following describes a device used as an experiment apparatus.

BRIEF DESCRIPTION OF DRAWINGS

FIG. 1 is a schematic view of a device according to the invention.

FIG. 2 is a basic circuit diagram of the spark generator.

FIG. 3 is a circuit diagram of the measuring part of the device designated in FIG. 1 by 13 and 15 or 14 and 16 respectively.

FIG. 4 is an enlarged schematic view of the parts according to the invention.

FIG. 5 is a side elevation of the experimental apparatus.

FIG. 6 is an enlarged view of the left part of FIG. 5.

FIG. 7 is a view of the parts shown in FIG. 6 in direction of arrow VII, and

FIG. 8 is a diagram showing for several methods the mean standard deviation (percent) in relation to the analytical gap (mm).

DESCRIPTION OF PREFERRED EMBODIMENT

On the optical bench 21 of a spectrometer, for instance a multichannel spectrometer, two spark discharge electrodes 2 and 3 are mounted in the optical axis 1. Electrode 2 is a carbon rod electrode of approximately 6 mm diameter whose end is a truncated cone of 9.5 mm of height and having a semispherical end surface with a radius of 1.6 mm. Electrode 3 located beneath electrode 2 is a circular carbon disk electrode with a diameter of approximately 12.5 mm and a thickness of approximately 5 mm, which has a central bore of 3.18 mm. The free gap between electrodes 2 and 3 is 2 mm; the center of the thus created spark discharge region coincides roughly with the optical axis 1 of the spectrometer. Electrodes 2 and 3 are held by a rider stand located on optical bench 21. Electrode 2 is clamped by a screw 23 to an arm 24 of the stand, the arm having an intermediate piece 25 of insulating material. The holder of electrode 3 consists of a plate 26 with an insulated mount 27, which carries a bearing 28 for a shaft 4 of carbon rod on whose slightly conical end is located the circular disk electrode 3 with its above-mentioned bore. Inside of bearing 28 shaft 4 carries a sliding contact ring against which a carbon brush 31 is pressed in the usual manner by means of a screw bushing 30. Under plate 26 is mounted a drive motor 32 whose driven pulley 33 is connected with a

drive pulley 35 on shaft 4 via an endless belt 34. This drive gives electrode 3 a steady rotation of 20 r.p.m..

Stand 1 also carries on another arm 36 an atomizer 37 for the production of an aerosol from the solution to be analyzed. It is a condensing chamber atomizer in which the specimen solution, which is drawn from a beaker via a suction tube 38, is not applied directly to where it is needed via an atomizer jet 40, but is atomized in a chamber, from which the thus created aerosol is ducted. An outlet 41 from the condensing chamber is provided with a siphon 42 and an overflow 43. FIGS. 6 and 7 also show an inlet tube 45 for the specimen solution, fastened in the condensing chamber by a screw 44, and a compressed air supply pipe 47 to the atomizer jet 40 provided with a hose connection 46.

The outlet duct ends in a jet 5 which is directed radially at the convex surface of the disk electrode 3 approximately in the second quarter behind electrode 2. The jet has an inside diameter of 2.4 mm and is located at 10–15 mm from the convex surface of the electrode 3.

The electrodes 2 and 3, via a terminal 48 attached to arm 24 and cable 49 and via terminal 50 attached to bearing 28 and cable 51 respectively, are connected with a high voltage spark generator according to Feussner, the circuit diagram of which is shown in FIG. 2. R represents an adjustable resistor, T a high voltage transformer, C₁ a capacitor, I an induction coil, SD a rotary switch running synchronously with the mains frequency, S a safety gap, Z a high ohmic resistor serving for ignition, and F the sparking gap between the electrodes 2 and 3. The spark generator operates with 12 KV effective voltage, 24nF capacitance and 0.02 mC inductance.

On rider stands 52 with lens mounts 53 are located as light guides a condensing lens 6 (UV-Achromat), a diaphragm 7, a lens 8, and a lenticulated condenser 9 on the optical axis 1 of the spectrometer. Behind this are arranged a spectrometer 10 with one exit slit each for the element line to be measured as well as an internal standard line and a photomultiplier 11 and 12 each for these two lines of analysis. The photomultipliers 11 and 12 each are connected to integrators 13 and 14 respectively and an impedance transformer and voltage meter 15 and 16 respectively. Parts 13 and 15, and 14 and 16 respectively which are shown in FIG. 2 as blocks, are interconnected as in the wiring diagram shown in FIG. 3. Here SEV represents the outputs of the photomultiplier 11 and 12 respectively, C₂ are two capacitors, O an operational amplifier and G a galvanometer. E, L and M show the switch positions for "discharge," "charge" and "measure."

The device is used in the following manner: The exit slits of spectrometer 10 with the respective photomultipliers 11 and 12 are aligned to the wavelength of the element line and the corresponding internal standard line respectively. The drive of the disk electrode 3 is switched on, the condensing chamber atomizer activated with an operating pressure of 2.2 atmospheres. The specimen solution, to which has been added, in addition to the element to be analyzed, a corresponding reference element in predetermined and constant concentration, is transformed into an aerosol by the atomizer 37. Because of the condensing chamber, in which the larger droplets settle, the aerosol achieves an especially high degree of fineness. Through jet 5 it is sprayed onto the convex surface of the disk

electrode 3, where it forms an even film which dries on its way to the discharge zone. With the capacitors C₂ being short-circuited (position E in FIG. 3) the spark generator is switched on and the spark discharge between the electrodes 2 and 3 is activated. As it passes through the discharge zone the material applied to electrode 3 vaporizes. The atoms thus created are excited and emit the spectrum characteristic for the specimen. The emitted light falling on the intermediate condensing lens 6 is projected especially evenly onto the spectrometer because of the intermediate projection device consisting of parts 6–9. When after approximately 100 seconds after the beginning of the spark transition a state of equilibrium is reached, an integrating measurement is started by switching capacitor C₂ to position 2. During a certain amount of time, which usually amounts to 1 min., but which can be extended up to 5 min. to determine especially small concentrations, for instance, without impairing the reproducibility, the photoelectric currents supplied by the multipliers 11 and 12 are stored in the capacitors C₂. Then the spark generator is switched off and the voltages of the capacitors C₂ achieved during charging, which are proportional to the corresponding line intensities, are measured by means of the impedance transformers and the voltage meters 15 and 16. The quantitative evaluation follows as usual by comparison of the measured voltages on the basis of previously established standards obtained with solutions of known concentration.

How much more accurate an analysis according to the invention can be in comparison to other known methods is shown in FIG. 5 which depicts the standard deviations over the analytical gap obtained from 30 runs each. The results marked with a circle were obtained according to Scheibe-Rivas, the results marked with a triangle according to Pagliassotti-Porsche, the values marked with white squares were obtained according to the invention with an atomizer without condensing chamber and the black squares represent the values obtained according to the invention with a condensing chamber. The curves show clearly that the device according to the invention even without the condensing chamber adds significant increase in accuracy and also a decreased dependence on the analytical gap than the so far reportedly most accurate method according to Pagliassotti-Porsche; further a device according to the invention with a condensing chamber atomizer reduces the analysis error expressed at standard deviation in comparison to the present state of technology by one tenth and it operates independently of the analytical gap within the range of 1–4 mm.

What we claim is:

1. In a device for quantitative spectrochemical analysis of a solution, comprising: two spark-discharge electrodes (2;3) defining a spark discharge zone, one of which electrodes has the form of a disk (3) and is provided with a drive; and a means for applying the solution in the form of an aerosol to the periphery of the disk, the improvement residing in that the said means include an atomizer for producing a flow of aerosol from the solution and have means to arrest relatively large droplets from the aerosol, and a nozzle disposed outside said spark discharge zone for directing the flow of aerosol at the disk (3).

2. A device according to claim 1 in which said means to arrest relatively large droplets from the aerosol comprises a condensing chamber.

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3. A device according to claim 1 in which the nozzle as seen in a direction of rotation of the disk (3) is directed at and disposed adjacent to the second quarter of the disk periphery located outside the spark discharge zone.

4. A method of performing spectral analysis of a solution by supplying the solution in the form of an aerosol into a spark discharge gap and examining the spectrum emitted by the spark discharge, comprising: arranging a spark discharge gap between a conducting rotatable disk and proximate elongate counter electrode; atomizing the solution into the form of a aerosol to be fed in

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a predetermined manner to the spark discharge gap; arresting relatively large and liquid particles of the aerosol; and feeding the aerosol devoid of said relatively large and liquid particles, into the spark discharge gap on the disk periphery from a region away from the spark discharge gap, whereby the aerosol becomes substantially dry when reaching the spark discharge gap and is devoid of heavy particles, thereby improving the accuracy of results of the spectral examination.

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