

March 21, 1944.

R. E. NUSBAUM ET AL

2,344,719

SPECTROCHEMICAL ANALYSIS METHOD

Filed June 4, 1942

3 Sheets-Sheet 1

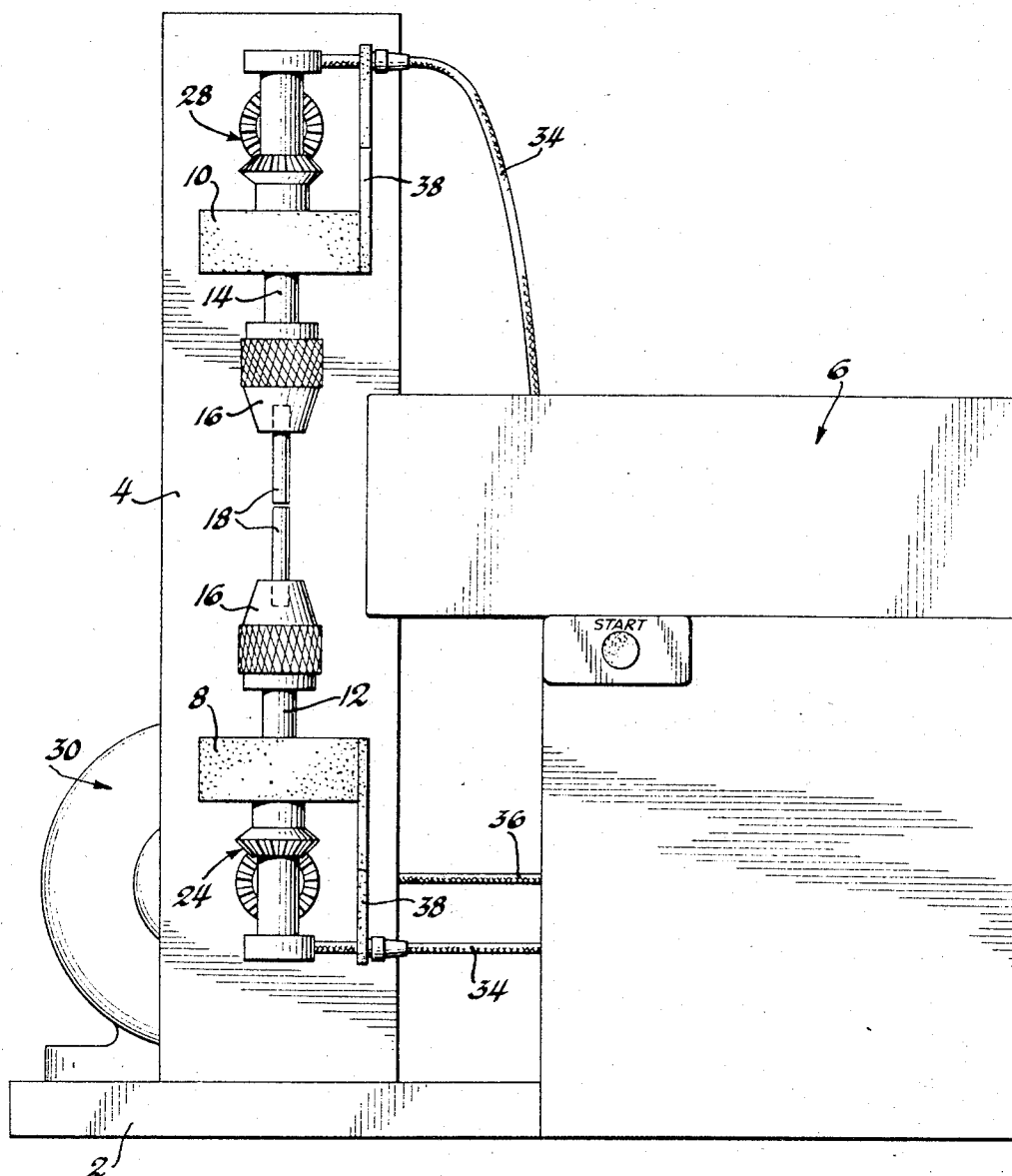


Fig. 1

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March 21, 1944.

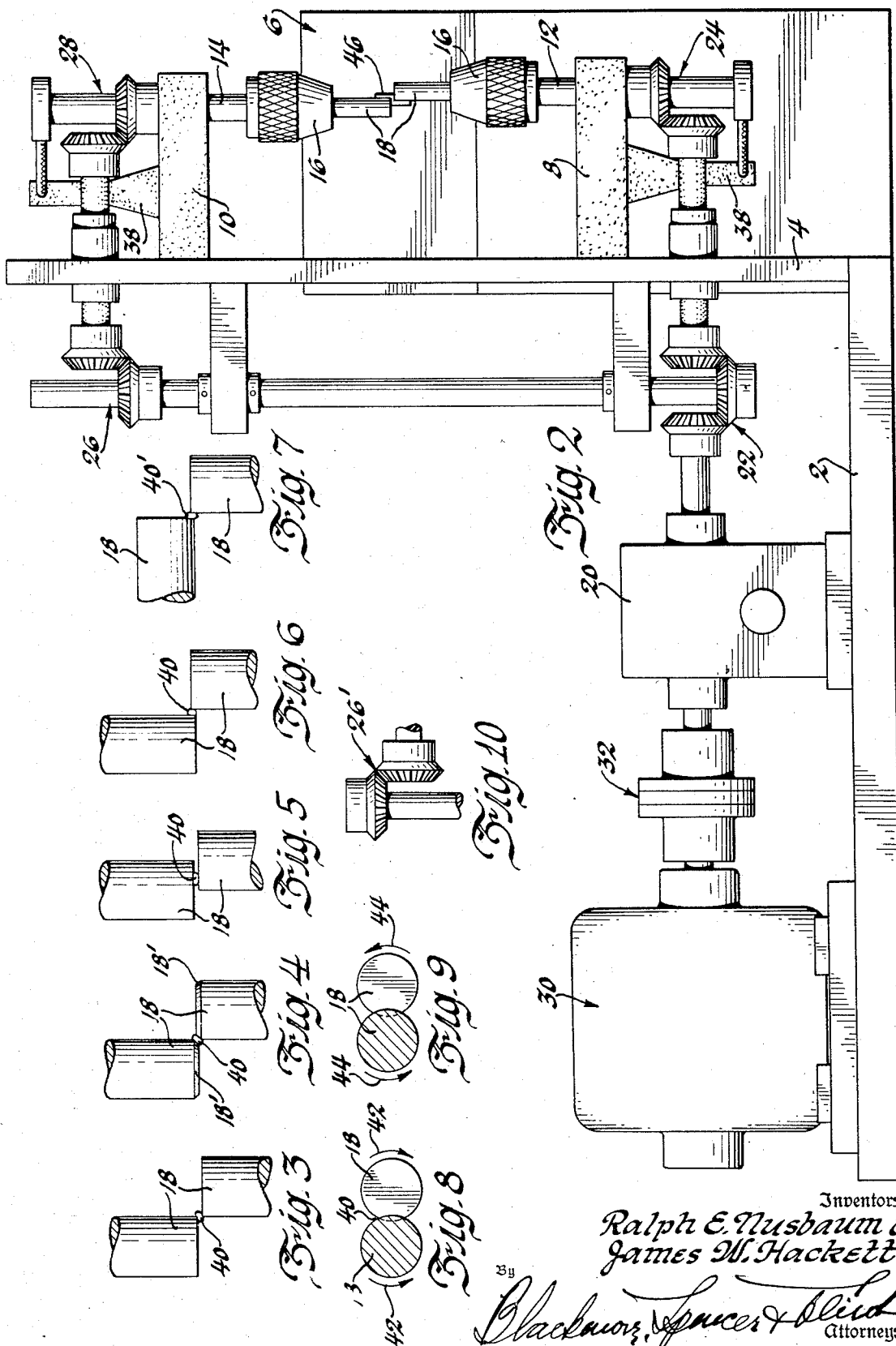
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SPECTROCHEMICAL ANALYSIS METHOD

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3 Sheets-Sheet 2



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SPECTROCHEMICAL ANALYSIS METHOD

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3 Sheets-Sheet 3

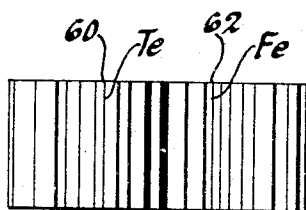
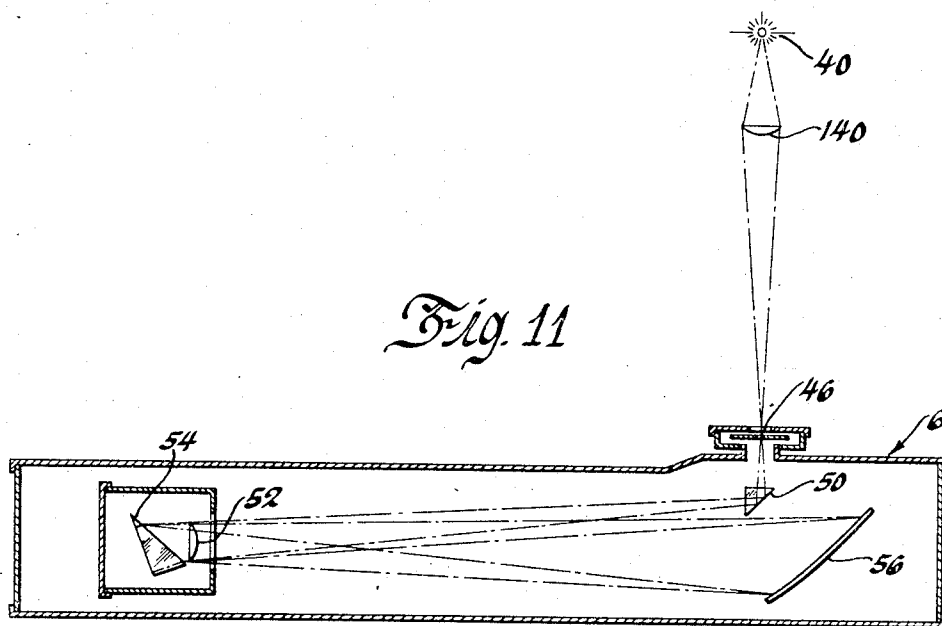


Fig. 12

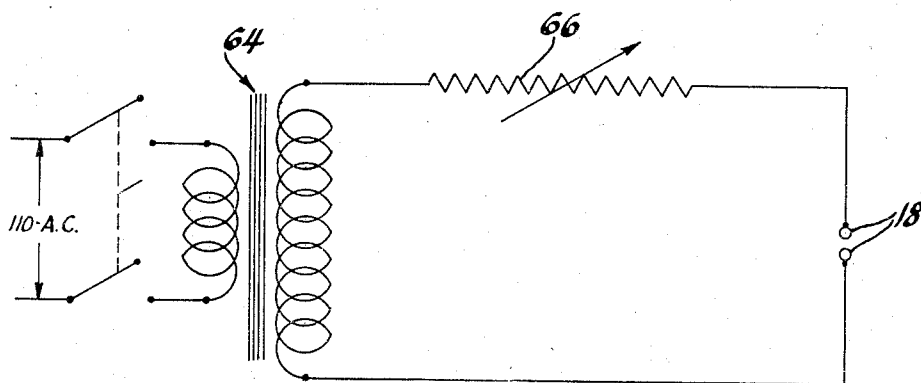


Fig. 13

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UNITED STATES PATENT OFFICE

2,344,719

SPECTROCHEMICAL ANALYSIS METHOD

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Application June 4, 1942, Serial No. 445,752

3 Claims. (Cl. 88—14)

This invention relates to spectrochemical analysis, particularly to an improved practical method of quantitative spectrochemical analysis. Patents 1,979,964—Duffendack et al. and 2,043,053—Martin, disclose and claim methods of spectrochemical analysis to which this invention relates.

A major problem in quantitative spectrochemical analysis has long been that of determining the amounts of elements present in test samples where these elements are present in such small quantities that they are readily vaporized so that the small quantities present are quickly burned away leaving only the elements which are present in large quantities and/or which are much less readily vaporized. This problem is present in acute form in the spectrochemical analysis of cast iron containing small amounts of tellurium.

We have solved the problem by providing a method whereby a constantly changing surface of the test material is presented to the excitation arc or spark. This is achieved by the expedient of striking the arc or passing the spark between samples of the test material at least one of which is continuously in motion. The test samples forming the electrodes are preferably substantially circular rods disposed before the spectroscope in such a manner that one or both may be rotated during excitation.

Figure 1 in the drawings shows a front elevation of apparatus which may be used in the improved process of our invention.

Figure 2 shows a side elevation view of the apparatus of Figure 1.

Figures 3 to 9 inclusive are detail views showing various dispositions of the electrodes.

Figure 10 is a detail of the apparatus of Figure 2 to show an alternative arrangement of one gear train of the apparatus.

Figure 11 is a diagrammatic view of a spectrograph such as may be used in carrying out the invention.

Figure 12 is a diagrammatic representation of the portion of the spectrum we have used in the analysis of tellurium iron alloys, and

Figure 13 shows a diagram of the electric arc circuit used in carrying out the invention.

Referring now particularly to Figures 1 and 2, we have indicated a base 2 having an upright member 4. The spectroscope or spectrograph 6 is mounted in cooperating relation with base 2 and member 4. Lower and upper bearings 8 and 10 are provided to support shafts 12 and 14 respectively, which rotate therein. The shafts 12 and 14 carry chucks 16

in which are secured electrodes 18 which are made of the material to be tested. Shaft 12 is connected to gear reduction unit 20 through gear trains 22 and 24, and shaft 14 is connected to unit 20 through gear trains 22, 26 and 28. Any suitable source of power 30, such as an electric motor, may be provided to supply power to gear reduction unit 20 through a suitable coupling such as the one indicated generally at 32. Electric power for the arc or spark may be supplied to electrodes 18 through brushes and slip rings by cables 34. Electric power may be supplied to the motor through cable 36. It will of course be understood that the necessary steps will be taken to insulate the brushes and slip rings from the frame and from each other. Such measures will include the provision of supports 38 of any suitable insulating material for the brushes.

Figure 3 shows the electrodes 18 so disposed as to rotate about substantially parallel axes, offset a distance approximately equal to the diameter of the electrodes. The arc or spark is indicated in Figure 3 as forming at 40. In Figure 4 the disposition of the electrodes is substantially the same as in Figure 3. In Figure 4, however, the peripheral edges of the electrodes have been chamfered as shown at 18'. Again, the arc or spark is indicated at 40. In Figure 5 the axes of rotation of electrodes 18 are not offset to the same extent that they are in Figures 3 and 4. In Figure 6 these electrodes 18 are offset even further than in Figures 3 and 4 and overlap axially somewhat, so that arc or spark 40 forms between the cylindrical surfaces of the electrodes rather than at the edges of the flat faces.

In Figures 3 to 6 inclusive, electrodes 18 are shown with their axes disposed substantially parallel. It is of course not necessary that they be so disposed. The electrodes may be disposed with their axes of rotation at right angles as indicated in Figure 7, with the arc or spark forming at 40'. If desired, the electrodes may be disposed with their axes of rotation at some angle between 90° and 180°—i. e., so that the relative position of the electrodes is somewhere intermediate the position of Figure 7 and any of the positions of Figures 3 to 6. Or, the electrodes may be disposed with their axes of rotation making an angle less than 90°.

In Figure 8 we have indicated by arrows 42 the preferred direction of rotation of the electrodes for the dispositions of Figures 3 to 6. In this preferred method, one of the electrodes rotates counterclockwise and the other rotates clockwise, with the result that, in the region

where the two electrodes are closest together, the edges of the two electrodes are moving in the same direction. When the electrodes are rotated in that manner, we have found that the arc or spark 40 forms at the "breaking point," or point of separation, of the region of overlap. The electrodes are preferably so disposed and rotated that this breaking point will be nearest the light-admitting aperture of the spectroscope. In that situation, unburned metal moves toward the arc and toward the spectroscope. To obtain those conditions for the disposition of electrodes shown in Figure 7, the horizontal electrode is rotated counterclockwise as seen from the right, and the vertical electrode is rotated clockwise as seen from above.

It should be understood that the direction of rotation of the electrodes shown in Figure 8 is the preferred form of practicing the invention. However, in the electrode arrangements of Figures 3 to 6, both electrodes may be rotated in the same direction to practice the invention. This method is shown in Figure 9, in which electrodes 18 both rotate counterclockwise as seen from above; the direction of rotation is indicated by arrows 44. Figure 10 shows a gear train 26' which could be substituted for the gear train 26 of Figure 2 to effect rotation of the electrodes as shown in Figure 9.

In most instances it is desirable to employ samples which have not previously been burned. This we have found to be the best method where the tellurium concentration is low, i. e., on the order of 0.001 to 0.005%. For higher percentages it might be preferable to preburn the electrodes so that the arc has played on all portions of the electrodes for a short time before the exposure of the spectrum is begun. With higher percentages of tellurium this technique might show greater reproducibility of conditions in the arc. The electrode rotation still has the advantage that the material in the arc is continually renewed and that errors which might arise from segregation of the tellurium in restricted areas on the electrode are avoided.

We have also found that the intensity of the tellurium lines varies with time. The intensity is normally highest at the beginning of the excitation, dropping sharply for a short period, e. g., 30 seconds, and then continuing at a fairly constant rate for another short period, and thereafter dropping off more slowly. For low percentages we have found it necessary to make the exposure at the beginning of the excitation to gain sensitivity. For higher percentages where maximum sensitivity is not required it might be desirable to take the photographs during the period of substantially constant intensity.

Figure 11 shows the elements of a suitable spectrograph, in front of which are or spark 40 is produced. Light from arc 40 may be condensed by lens 140 and passed through slit 46 to a prism 50 which directs the light through lens 52 on to refracting prism 54, the light then passing again through lens 52 and falling upon a screen 56, which may conveniently be a piece of photographic film.

In Figure 12 we have reproduced diagrammatically a portion of a spectrogram of iron containing a small amount of tellurium. We have found it convenient to use that portion of the spectrum shown, but other portions thereof can likewise be used to practice the invention. It will of course be understood that the spectroscope used should give good lines and should have adequate resolv-

ing power. For that portion of the spectrum shown, it should have sufficient resolution to resolve the tellurium line at 2385.76 Angstrom units from the two adjacent iron lines at 2385.95 and 2385.58 Angstrom units.

It is contemplated that the internal standard method of analysis will be used to ascertain the percentage of tellurium in the sample. This method of analysis is described and claimed in the above-mentioned United States patents, 1,979,964—Duffendack et al. and 2,043,053—Martin. In Figure 12, the Te line 60 at 2385.76 Å. is the analysis line, and the Fe line 62 at 2380.0 Å. is the internal standard line.

Figure 13 shows an electrical circuit which may be used to produce the excitation arc in practicing the invention. A 110 volt A. C. source is indicated. The voltage is stepped up by transformer 64 to a suitable potential. Potentials of from 2000 to 5000 volts have been used, and the arc current has been successfully varied from 0.5 to 5.0 amperes. A high ballast variable resistance 66 combining high current carrying capacity and high insulation should be used.

We have found that the high voltage A. C. arc tends to provide a combination of the properties of the high sensitivity of the D. C. arc and the reproducibility of the electric spark. It resembles the D. C. arc because a relatively large amount of sample is vaporized and it resembles the spark because the arc is continuously being reestruck and also because a high voltage is involved. It is possible that for samples where high sensitivity is not required the spark would be preferred. In some cases it may be desirable to employ a D. C. arc.

In some cases it may be satisfactory to rotate one electrode only. If desired one electrode only may be of the composition to be analyzed, the other being of some material of known analysis which will not interfere with the analysis of the element desired.

The invention may be employed in analyses for various elements besides tellurium. It is equally applicable to analyses of solid solutions and physical mixtures. Best results have been obtained with solid samples. The method may, in some cases, be advantageous when analyzing liquids, this usually being accomplished by saturating a conducting electrode, for example a carbon electrode, with the liquid to be analyzed.

We claim:

1. The method of quantitative spectrochemical analysis of metal alloys or mixtures for tellurium or other elements present in low concentration and which vaporize rapidly in the arc, which consists in preparing electrodes in the form of rods, at least one of which comprises the material to be analyzed, mounting the rods with their axes displaced and with portions off of the axes most closely adjacent each other, rotating the rod comprising the material to be analyzed while causing an electrical discharge to pass between the adjacent portions of said rods to thereby present fresh unmelted metal to the arc so as to replenish the supply of the relatively volatile element, recording on a photographic medium a selected spectral line of said element and of a control element present in the material to be analyzed, and determining the amount of said element in said material by comparing the ratio of opacities of said lines with the ratio of opacities of the same lines obtained in the same manner from samples containing known quantities of said element.

2. The method of quantitative spectrochemical analysis of metal alloys or mixtures for tellurium or other elements present in low concentration and which vaporize rapidly in the arc, which consists in preparing electrodes in the form of cylindrical rods comprising the material to be analyzed, mounting the rods with their axes displaced and with portions off of the axes most closely adjacent each other, rotating the electrodes while causing an electrical discharge to pass between the adjacent portions of said electrodes to thereby present fresh unmelted metal to the arc so as to replenish the supply of the relatively volatile element, recording on a photographic medium a selected spectral line of said element and of a control element present in the material to be analyzed, and determining the amount of said element in said material by comparing the ratio of opacities of said lines with the ratio of opacities of the same lines obtained in the same manner from samples containing known quantities of said element.

3. The method of quantitative spectrochemical analysis of metal alloys or mixtures for tellu-

rium or other elements present in low concentration and which vaporize rapidly in the arc, which consists in preparing electrodes in the form of cylindrical rods comprising the material to be analyzed, mounting the rods with their axes displaced and with portions off of the axes most closely adjacent each other, rotating the electrodes in opposite directions while causing an electrical discharge to pass between the adjacent portions of said electrodes to thereby present fresh unmelted metal to the arc so as to replenish the supply of the relatively volatile element, recording on a photographic medium a selected spectral line of said element and of a control element present in the material to be analyzed, and determining the amount of said element in said material by comparing the ratio of opacities of said lines with the ratio of opacities of the same lines obtained in the same manner from samples containing known quantities of said element.

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