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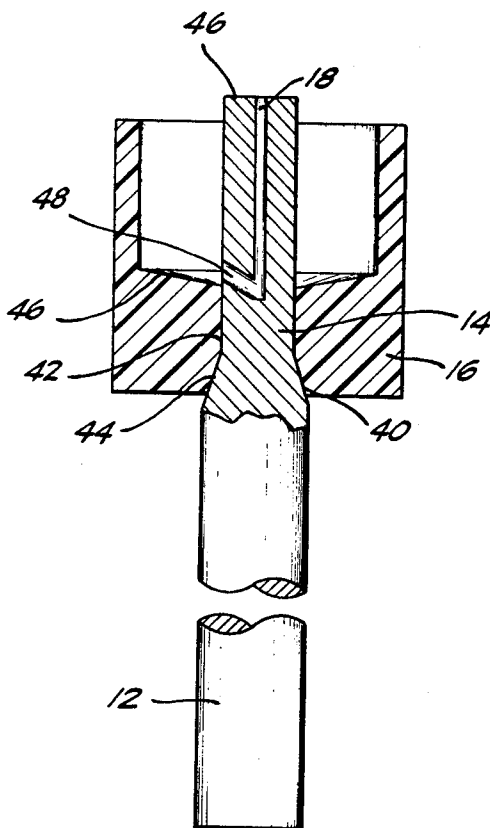
[54] **ELECTRODE**
4 Claims, 2 Drawing Figs.

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 313/217, 313/356, 315/111
 [51] Int. Cl. **H01J 17/26**
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 356; 315/111; 356/86

[56] **References Cited**
OTHER REFERENCES

"A 'Vacuum Cup' Electrode for the Spectrochemical Analysis of Solutions" by Theodore H. Zink, **APPLIED SPECTROSCOPY**, Vol. 13, No. 4, pp. 94—97 (1959). Class 356—86

ABSTRACT: An improved vacuum cup electrode for spectrographic analysis is described wherein a generally flat surface is provided at the gap end of the electrode rather than the conventionally employed rounded end or hemispherically shaped end. It has been found that this flat tip electrode improves the sensitivity and reduces the necessary exposure time for spectrographic analysis of samples. The electrodes comprise cylindrical rods having an upper portion of reduced diameter with a longitudinal capillary bored through the upper section and communicating with a radial passageway at the base of the reduced diameter upper portion. The sample cup is used in combination with the electrode to retain a liquid solution sample about the upper portion of the electrode to permit the solution to feed into the radial passageway and be drawn up the capillary during use of the electrode.



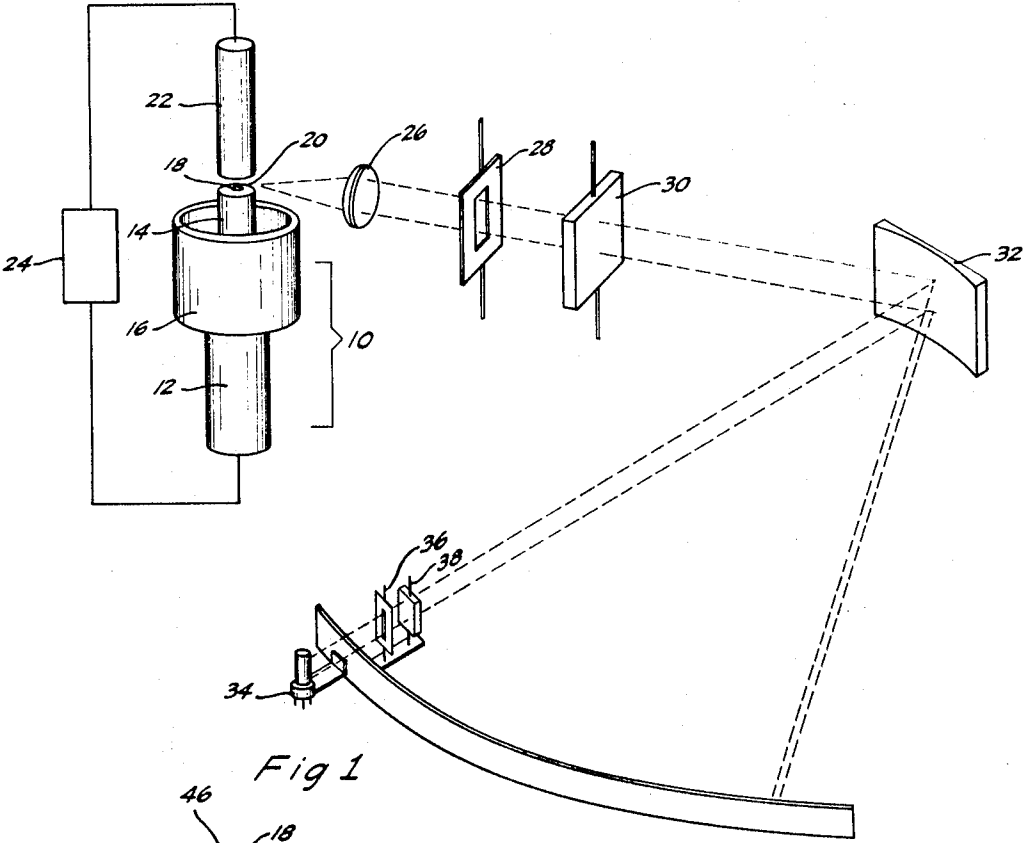


Fig 1

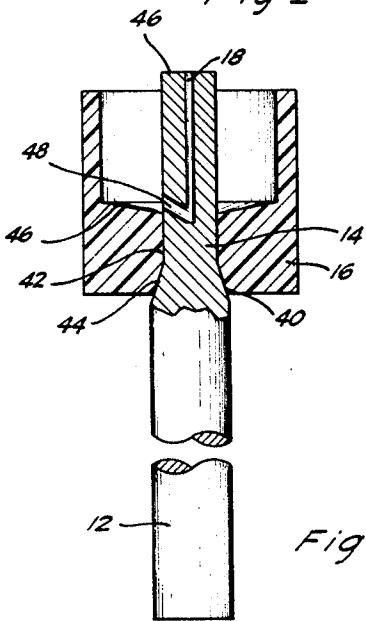


Fig 2

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ELECTRODE

DESCRIPTION OF THE INVENTION

This invention relates to an improved electrode and in particular relates to improvements in vacuum cup electrodes used for emission spectroscopic analyses.

In emission spectroscopy, samples of material being analyzed are supplied to an electrical spark maintained in an air gap between two electrodes and the resulting decomposition of the sample emits radiant energy characteristic of the sample under investigation. When solutions of samples are analyzed, various methods have been proposed to provide a continuous introduction of the solution into the air gap between the electrodes. One of the most successful techniques which has been developed comprises use of a vacuum cup electrode as described by Theodore H. Zink in "Applied Spectroscopy," Vol. 13, No. 4, pages 94-97 (1959). In this technique, an electrode is used which has a longitudinal capillary in its upper end that communicates with a radial passageway intermediate its length and a plastic sample cup or holder surrounding the upper portion to permit solution from the cup to enter the radial passageway. The solution is transferred into the analytical gap for excitation by means of the reduced pressure created in the air gap with each discharge pulse and thereby a continuous supply of sample is assured. These electrodes have been supplied with rounded or hemispherically shaped tips to permit drainage of excess sample from the spark gap as described in the aforementioned article.

I have now found that a significant increase in sensitivity of emission spectroscopy as well as a substantial saving in time for the analysis can be achieved by providing vacuum cup electrodes having generally flat-surfaced spark gap ends. Preferably, the generally flat surface tip is perpendicular to the longitudinal axis of the electrode, however, slightly inclined tips can also be employed if desired.

The invention will now be described by reference to the FIGS. of which FIG. 1 illustrates the electrodes and sample holder in a typical grading spectrometer; and FIG. 2 illustrates in greater detail the structure of the improved vacuum cup electrode.

Referring now to FIG. 1, the vacuum cup electrode is illustrated at 10 having a base 12 with an upper portion 14 of slightly reduced diameter. The upper portion is surrounded by a cup-shaped sample holder 16 and a small capillary 18 extends longitudinally from the upper flat surface 20 of the electrode to a point near the base of the upper portion as will be described in greater detail hereinafter. The other electrode 22 is shown above the vacuum cup electrode and the electrodes are connected to a suitable source of electrical energy 24 to provide any of a variety of electrical excitation for the sample in the spark gap. The voltage supply means 24 are sufficient to provide a high voltage AC spark across the air gap between the electrodes, a DC arc between the electrodes, a high voltage AC arc, a low voltage AC arc, or a unidirectional DC arc in accordance with the conventional practice in emission spectroscopy.

The emission from the excited sample is passed through various means for focusing and diffracting the various wavelengths or frequencies of emissions to obtain a determination or quantitative measure of the characteristic emission for the sample. Visual, qualitative measure as in a spectroscope can be used. The quantitative measurement can be by way of a photographic film as in a spectrograph, or can be measured electrically by various means such as a photomultiplier tube as in a spectrometer. Various methods can be used for separating the sample emission into each of its component wavelengths, e.g., a prism can be used as in a conventional refraction instrument or a grating can be used as in a conventional diffraction instrument. Such gratings can be either the transmission or reflective type gratings.

FIG. 1 illustrates use of a reflective grating in a spectrometer and, in this illustration, the emission from the sample is

passed through a collimeter lens 26, an entrance slit 28 and an entrance refractor plate 30 which can be adjusted to compensate for wavelength changes caused by variations in ambient temperatures. The sample emission then falls on a reflective grating 32 which diffracts the emission into sharply defined emissions having wavelengths from about 2,000 to 8,000 Angstroms which are focused against a series of photomultiplier tubes 34 that are arranged on a focal curvature to the grating and which measure particular wavelength emissions. The emissions are further focused by exit slit 36 and exit refractor plate 38.

Various methods can be employed for obtaining a measurement of the intensity of the emission falling on each of the photomultiplier tubes that are positioned along the focal curve. In a particular embodiment, the photomultiplier output can be used to charge a capacitor so that at the end of the exposure the charge on the capacitor is proportional to the integrated intensity of the light for that particular wavelength. The charge on the capacitor can thereafter be measured by various techniques to determine the quantitative emission; in one particular commercial application the charge on the capacitor is determined by measuring the number of times that the charge can be used to charge a smaller standardized capacitor and this frequency of charging appears as a 4-digit number in a direct readout counter on the instrument. A common method of calibrating the read out of such an instrument is to add a known amount of a standard material to the sample under investigation. The analysis of the sample under investigation is thereafter continued until the read out value for the emission characteristic of the added material reaches a predetermined level.

FIG. 2 illustrates the improved vacuum cup electrode of this invention in greater detail. The electrode is shown as a generally elongated body of spectroscopically pure graphite having a lower portion 12 of slightly greater thickness than the upper portion 14. Preferably, cylindrical stock is employed for these electrodes, however, it is within the scope of the invention to use stocks of varied cross-sectional shapes and sizes. The upper portion 14 of the electrode meets the lower portion in a shoulder which can be inclined as shown at 40. This shoulder comprises the support means for the sample cup 16 which has a central bore 42 for receiving the upper portion of the electrode and a tapered seat 44 which mates with and seals against the shoulder 40. Cup 16 can be formed of any suitable material, e.g., Teflon, graphite, etc., preferably an inert plastic such as Teflon is employed. The interior bottom of the cup can slope inwardly as shown at 46 to permit the sample to drain adequately into the center of the cup from which it can be supplied to the capillary solution supply means interior of the upper portion of the electrode. The capillary supply means comprises at least one longitudinal capillary 18 which passes from the upper flat surface 46 of the electrode to a point intermediate its length. This capillary can be of a diameter, in inches, from about 0.0135 (No. 80 drill) to about 0.052 (No. 55 drill); preferably from about 0.024 (No. 73 drill) to about 0.032 (No. 67 drill); and should extend to approximately the base of the interior of cup 16. With most commercial vacuum cup electrodes, the length of this passageway can be made from 0.3 to about 0.8, preferably from 0.5 to 0.7 inch. The upper end of the electrode preferably extends from about 0.1 to about 0.5 inch above the upper rim of cup 16.

At least one radial passageway 48 is provided which communicates from the exterior of the electrode to the base of the longitudinal passageway 18. This passageway permits the solution containing the sample under investigation to drain into the capillary tube for lifting into the air gap at the upper surface 46 of the electrode.

The electrodes as illustrated are generally from about 1 to about 3 inches; preferably about 2 inches in overall length; and the length of the upper portion 14 is from about one-half to about 1; preferably about three-fourth inch in length. The diameter of the lower portion 12 is generally from about 0.2 to about 0.4; preferably about 0.25 inch and the diameter of the

upper portion 14 is from about 0.1 to about 0.2 inch, preferably about 0.18 inch. With these dimensions, the vacuum cup electrode as thus described will fit the conventionally employed emission spectra apparatus.

To illustrate the results obtainable by the application of my invention, various electrodes shaped with the flat upper surface as illustrated in FIG. 2 were employed and compared to the use of the conventional hemispherically tipped vacuum cup electrodes in a conventional spectrometer using a 5.6 amp, 5 breaks per half cycle, spark-excited, air-quenched, high voltage, alternating current spark source for excitation of the sample. The flat-tipped electrodes, according to this invention, had a capillary length of 0.59 inch while the conventional hemispherically shaped vacuum cup electrodes used as a comparison had a capillary length of 0.67 inch. The electrodes were used for the analysis of two standard solutions, a high range and a low range solution, having the following compositions:

Component	Solution Concentration— Parts Per Million	
	High Range	Low Range
Copper	16	4
Iron	40	10
Nickel	20	5
Vanadium	32	8
Cobalt*	80	80

*Cobalt was used as the internal standard.

In the comparative experiment, the sample cup was filled with 2 milliliters of the test solution and the instrument was preparked for 40 seconds before introducing the sample. The sample was introduced and the electrodes were sparked for the necessary time for the counter to read 6,000 units for the cobalt internal standard at a wavelength of 3,502.3A. This value was the calibration count for the cobalt internal standard that had been added to the solution at a concentration of 80 parts per million. With the instrument at the high calibration range, the counting time required to produce this minimum cobalt calibration count averaged 30 seconds for the flat-tipped electrodes as contrasted to 52 seconds for the rounded or hemispherically shaped conventional vacuum cup electrodes. The signal to noise, i.e., the intensity of the line to the background, on the nickel and vanadium determinations was approximately 1.65 times greater than that observed with the hemispherically shaped conventional vacuum cup electrode. At the low calibration range, the exposure time for reaching the calibration count for the internal cobalt standard were 26 seconds for the flat-tipped electrodes and 45 seconds for the conventional hemispherically shaped electrodes. Again, the flat-tipped electrodes gave a greater reading having an intensity of line to background factor which was approxi-

mately 2 times greater than that observed with the hemispherically shaped electrodes.

In an additional experiment, some of the flat-shaped electrodes used in the preceding experiment were removed and the upper surfaces were rounded to provide hemispherically shaped tips on these electrodes, characteristic of the conventional vacuum cup electrode. This modification provided the flat-tipped and hemispherically shaped electrodes with identical capillary lengths, i.e., 0.59 inch. The comparative experiments were repeated and it was found that the flat-tipped electrodes again provided better sensitivity with the necessary time to reach the calibration count for the internal cobalt standard being 38 seconds as opposed to 65 seconds for the hemispherically shaped electrodes. The net response for the electrodes in this experiment is set forth in the following table:

Electrode	Copper	Iron	Nickel	Vanadium
Flat-tipped.....	5,200	7,100	6,220	6,800
Rounded tip.....	5,300	5,620	5,300	5,600

It can be seen from the preceding data that the use of the flat-tipped electrodes produced a greater sensitivity of the instrument to the analysis for the aforementioned metals as well as providing the aforementioned reduced time to reach the necessary count for the cobalt internal standard.

While the invention has been described with regard to a particularly illustrated embodiment thereof, it is understood that the invention also encompasses obvious equivalents of structure and materials.

I claim:

1. In a vacuum cup electrode for spectrographic analysis wherein an elongated body formed of spectroscopically pure graphite is provided with at least one longitudinal passageway extending from its upper end to a point in its upper portion and at least one radial passageway extending from the periphery of said body to communication with the lower end of said longitudinal passageway with support means on said body beneath said radial passageway to support a sample container about the upper end of said body, the improvement comprising a generally flat surface at the upper end of said electrode.

2. The electrode of claim 1 wherein said generally flat surface is perpendicular to the longitudinal axis of said body.

3. The electrode of claim 1 in combination with an upright cup-shaped sample container supported on said body and surrounding the upper end thereof.

4. The electrode of claim 1 wherein said upper portion of said body has a lesser thickness than the lower portion thereof and said support means comprises a shoulder between said upper and lower portions.