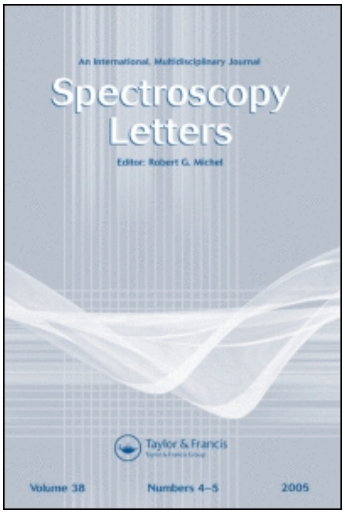

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Trace Analysis of Nonconducting Materials by a Spark Source Mass Spectrographic Auxiliary Electrode Method

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TRACE ANALYSIS OF NONCONDUCTING MATERIALS BY A SPARK SOURCE MASS SPECTROGRAPHIC AUXILIARY ELECTRODE METHOD

KEY WORDS: spark source, mass spectrographic, analysis, auxiliary electrodes, nonconductors

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INTRODUCTION

The survey analysis capabilities of spark source mass spectrography have proved to be very important in the determination of very low concentrations of elements in nonconductors and semiconductors. Some of the methods devised for the special handling and sparking of the poor conductors have been reviewed by Guthrie[1]. In general, attempts to initiate and sustain a radio frequency spark between nonconductor self-electrodes require inconviently high spark voltages and considerable operator time and attention. Moreover, the low ion yields often characteristic of the nonconductor self-electrode spark compel exposure times commonly in excess of one hour for exposure levels requisite for the detection of impurities at 1 part-per-million concentrations.

Ahearn[2] and James and Williams[3] have devised sparking techniques that placed two self-electrodes in very close proximity to conducting electrodes so that random sparking to the nonconductor produced representative ions. However, the uncontrolled production of conductor ions necessitated construction of special ion beam monitors in order to correct exposure ratios of impurity ions with the sample matrix ions. The pressed

electrode method with graphite[4] has gained considerable popularity among spark source mass spectroscopists during the past six years. Although the graphite electrodes enable internal standardization and a spark that demands little operator control, the method suffers from numerous undesirable characteristics, such as sample prehandling, a dilution of impurities that requires longer exposures to produce equivalent plate darkening, possible spectral interferences from the many ionized carbon species generated in the spark, and high fog levels on the low-mass region of the photographic plate. Other pressed electrode techniques, to various degrees, present the same problems.

This communication introduces an auxiliary electrode spark source mass spectrographic method for nonconductors that requires no sample prehandling nor dilution and provides spectra essentially characteristic of only the sample matrix and sample trace impurities. Vaporization and ionization of the sample are accomplished by sparking across a small surface region defined by two refractory metal auxiliary electrodes. The preliminary investigation results reported herein suggest that the method should be applicable to the analysis of numerous nonconducting materials.

EXPERIMENTAL

All exposures were made on Ilford Q-2 plates in an Associated Electrical Industries MS-7 double-focusing mass spectrograph. The analyser and source pressure were maintained at 10^{-9} and 10^{-7} torr, respectively. Photographic plates were developed with Eastman Kodak D-19 developer and processed in the customary fashion. Peak line transmission data were obtained from the photoplates with a National Spectrographic Laboratories microphotometer, and emulsion calibrations were determined by the standard Churchill two-line method. All measured exposures were corrected for fog and background.

The auxiliary electrode and sample arrangement in the source chamber is shown in Figure 1. A small piece of crystal, about 2 x 2 x 5 mm, was cleaved from a larger sample and mounted in a simple Ta-foil holder. Two Ta electrodes which were separated by about 0.5 mm were brought into contact with the electrically floating nonconductor. With KBr or KCl, a 15 or 20 KV spark started immediately upon contact of the auxiliary electrodes with the crystal and provided ions that were characteristic of the matrix salt and its impurities. After spark initiation, little attention to the sample and electrodes was required to maintain a regular rate of ion production. The Ta-foil shield prevented the build up of a conducting layer of material on the quartz insulator.

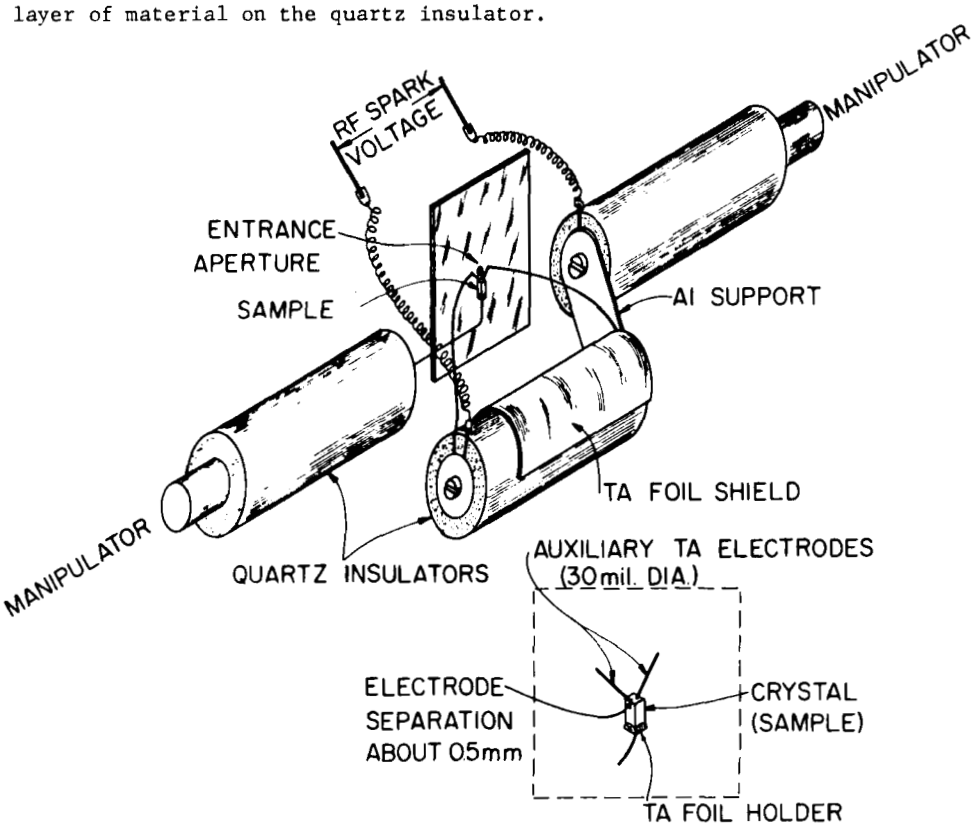

FIG. 1

MS-7 Source Arrangement for the Auxiliary Electrode Spark Mass Spectrographic Technique.

RESULTS AND DISCUSSION

The degree to which the Ta electrodes were sampled varied from exposure to exposure. However, comparisons of the $^{181}Ta^{+}$ and $^{180}Ta^{+}$ line intensities in exposures from Ta-Ta sparks with the appearances of the same lines from Ta-nonconductor sparks indicated that Ta consistently constituted less than 1% of the total ion beam. Since the total impurity concentration in the Ta wire was 6500 ppma (parts per million atomic), the electrodes contributed less than 65 ppma of trace impurities to the Ta-nonconductor spectrum. Generally, such a blank contribution will be negligible relative to the expected accuracy of a spark source spectrographic method. However, this contribution can be significant in cases in which a 65 ppma blank comes from only a few elements or in which sample impurities common to the electrodes are sought at concentrations below 1 ppma. The use of Ta of higher purity, or other high purity refractory metals, such as Re, Os, or W, should further reduce these trace level contributions from auxiliary electrodes.

The capability of this technique to provide accurate bulk analyses is illustrated by the trace level comparison data in ppmw (parts per million by weight) for KBr and KCl crystals shown in Tables 1 and 2, respectively. With the exception of the halogens, the mass spectrographic data represent the averages of triply determined relative concentrations referenced to $^{41}K^{+}$ of the matrix. Because of the similarities in ionization and sampling properties possessed by the halogens, the concentrations for these elements were based on either the Br or Cl of the matrix analyzed.

In Table 1, the reported Naval Research Laboratory (NRL) analyses of the doped KBr crystal were performed by flame emission and atomic absorption, neutron activation and chemical methods. With the exceptions of Ca, I, Na, S and Si, the agreement between the data sets is quite acceptable if

TABLE 1

Results from Auxiliary Ta-Electrode Analysis of a NRL, KBr Control Crystal

Element	Concentration (ppmw)	
	Auxiliary Electrode Method	NRL Analysis
Ag	2.8	2
Al	2	2
Ba	1.6	0.75
Ca	130	1
Cl	650	---
Cs	19	17.8
Cu	0.5	0.7
F	4.3	0.9
Fe	1.0	4
I	48	2
Li	0.007	0.1
Mg	1.2	1.1
Mn	0.1	1
Na	67	3.1
P	0.08	0.3
Pb	0.8	2.5
Rb	81	114
S	82	1
Si	22	1
Sr	0.9	7.7
Tl	2.4	---

the usually accorded accuracy of plus or minus an approximate factor of three is applied to the mass spectrographic data. The disparities in concentration values can be attributed to possible localized inhomogenieties in the segment of the crystal analyzed, selective volatilization and ionization by the spark or selective instrumental transmission of ions to the photographic plate.

TABLE 2

Results from Auxiliary Ta-Electrode Analysis of a Harshaw Optical-Quality KCl Crystal

Element	Concentration (ppmw)	
	Auxiliary Electrode Method	Semi-Quantitative Optical-Emission Spectrographic Method
Al	21	4
B	0.6	4-20
Br	540	---
Ca	1000	4
Cr	3.6	4
F	36	---
Fe	17	4
Mg	23	4
Mn	7.2	4
Na	900	4-20
Ni	2.8	4
P	3.7	---
Rb	4.3	---
S	380	---
Si	1700	4-20
Ti	430	2-8
V	28	4

In Table 2, the independent analysis of a Harshaw optical quality KCl crystal was accomplished by a semiquantitative standard-addition optical-emission DC-arc method[5]. Thus, the comparison of concentration data is less rigorous than that in Table 1. With the exceptions of Ca, Na, Si and

Ti, the general ability of the auxiliary electrode method to produce an accurate bulk analysis again appears substantiated. The disparities in the mass spectrographic concentrations are attributable to the reasons previously given.

Average precision for the measured concentrations was ± 44% relative standard deviation. This precision value primarily reflects sample inhomogeniety and lack of precise spark control, and is typical for replicate spark source analyses on similar samples. Ion current attenuation by beam chopping would be expected to increase sampling and improve precision.

In summary, the auxiliary electrode method presents a new means for the survey analysis of nonconducting materials that is simple, requires no sample prehandling, requires no secondary standards, does not force conduction by long segments of nonconductor, and provides a bulk analysis that has the accuracy and precision typical to the spark source mass spectrographic technique. Although the applications reported in this communication were limited to salt-like nonconductors, semiconductors and materials that do not form usable self electrodes, such as those that have low melting points and readily vaporize, should be amendable to this technique. Also, samples that normally occur as powders can be pressed into pellets and treated as solid crystals.

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