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APPLICATION OF LIQUID-LAYER SOLID-SAMPLE SPARK TECHNIQUE TO SPECTROCHEMICAL ANALYSIS USING CONVENTIONAL SPARK SOURCE

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION

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APPLICATION OF LIQUID-LAYER SOLID-SAMPLE SPARK TECHNIQUE TO SPECTROCHEMICAL ANALYSIS USING CONVENTIONAL SPARK SOURCE

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SUMMARY

Improved analytical results were obtained when a thin layer of water or aqueous solution was aspirated onto the surface of a flat metal sample during spark analysis. Studies with liquid layers applied to aluminum alloy standards demonstrated that increased sampling and line emission produced increased analytical curve slopes and count precision for the determination of impurities. Spark exposure times were reduced by one-half to one-fifth.

The solute from a solution layer was used to replace the aluminum internal standard in both the spark analysis of aluminum alloys and the dc arc analysis of the sample electrode material vapor deposited on the counter electrode.

In spark analysis when a liquid layer was applied, interfering emission from atmospheric elements and from the counter electrode material was minimized, and the physical appearance of the spark crater showed no oxide formation. Inductance of the spark circuit and aspiration rate influences were investigated. Application of this method to the analysis of refractory and superalloys is indicated by the results of the analysis.

INTRODUCTION

Investigations of standard analytical spark methods for solid and solution samples using submicrosecond time-resolved emission spectroscopy have recently lead to the development of new analytical techniques (refs. 1 and 2). One of these new techniques, which combines the solid point-to-plane approach with solution samples, is called the liquid-layer solid-sample spark method (ref. 2). This report discusses some further investigations of the liquid-layer solid-sample spark method using a conventional spark source.

In conventional spark analysis, the light from a spark passing between a smooth-surface metal electrode and a pin counter electrode is spectrally dispersed and measured. This electrode arrangement is commonly known as the point-to-plane method (ref. 3). The measured intensity of the dispersed light is related to the concentrations of constituent elements of the metal electrode sample.

In the liquid-layer solid-sample spark method, apparatus similar to that of the point-to-plane technique was employed with the addition of a means for applying a liquid layer to the surface of the metal electrode during the time the sample is being sparked. In this investigation, a thin layer of liquid, generally water or aqueous solutions, was applied by means of a simple aspirator.

The application of a thin liquid layer in the liquid-layer solid-sample spark method produced some significant changes in light intensity from the spark, which directly affected the analytical relation of light intensity to concentration. Substantial increases in light emission from sample electrode constituents were observed previously (ref. 2), and the ratio of spectroscopic line emission to radiation background was increased. The amount of sample electrode material displaced and the depth of penetration of the spark into the sample electrode was also increased. The area of the spark on the sample surface was free of oxides and discolorations, and the spark craters appeared clean and shiny for the wide variety of materials examined. These effects were verified in this investigation. In addition, the analysis was improved as a result of increased slope of the analytical curves due to the influence of these effects.

Previous investigations (ref. 2) have shown that when the liquid layer is an aqueous solution, the solute from the solution layer and the electrode material from the solid beneath the solution layer undergo identical processes in the spark discharge, which result in useful light emission from the solute for quantitative analysis. For example, solute emission was used to replace the emission from the major element of the solid sample as a constant concentration reference in analysis. As a result, wide concentration changes in alloys can be investigated and directly referenced to a common standard.

The results of applying the liquid-layer solid-sample spark technique to aluminum alloys using a conventional spark source are discussed in this report. Quantitative results are presented on the effect of liquid aspiration rate, inductance of the spark discharge circuit, and the precision of light emission from repeated sparkings. Also investigated was the vapor deposit of sample material on the counter electrode. The applicability of this method to refractory and superalloy analysis is indicated by the results of the analysis.

EXPERIMENTAL

In this investigation with the liquid-layer solid-sample spark technique, standard operating procedures were employed with the available spark source and spectrographic and spectrometric readout systems. The only required modifications were those of the sample holding apparatus.

Spark Source and Dispersive Methods

A commercially available spark source was used with a typical range of spark parameters of capacitance (0.0025 to 0.015 μf), inductance (residual to 1250 μh), and resistance (residual to 5 Ω). The spark source incorporates an air-interrupted secondary spark gap in series with the analytical spark gap. Unless otherwise specified, the operating parameters for these tests are given in the following table:

For the spark source,	
Resistance, ohm	residual
Inductance, μh	residual
Capacitance, μf	0.01
Discharge voltage, V	17 000
Discharges per cycle	4
rf current, amp	15
Prespark time, sec	0
Exposure time, sec	5 to 30
Analytical gap spacing, mm	5
Atmosphere	air
For the sample,	
Gallium solution concentration, percent	0.25
Silicon concentration in aluminum, percent	0.73
Aspirating gas	compressed air

Photographic and photoelectric detection of the same spark emission was obtained simultaneously using a 3.4 meter Ebert spectrograph (1200 line/mm grating) and a 1.5 meter Paschen-Runge direct reading spectrometer (1200 line/mm grating). Photographic measurements were made in support of the photometric data to determine background levels and line interferences.

Atomizer

A commercially available atomizer-burner, commonly used in flame photometry, was employed to supply a thin, reproducible liquid layer on the surface of the sample electrode. The fuel jacket of a medium-bore atomizer burner was removed and the remaining oxygen nozzle and burner base was mounted in the atomizer-burner holder. This unit was attached to a phenolic resin rod held in a ring stand for convenience of positioning and adjustment of the direction of the spray.

Sample Holder

A new sample stand was constructed for these tests. With the atomizer burner mount in place, the sample holder retains the aluminum solid electrode against three plastic alining screws by the upward pressure from a spring below the sample (fig. 1).

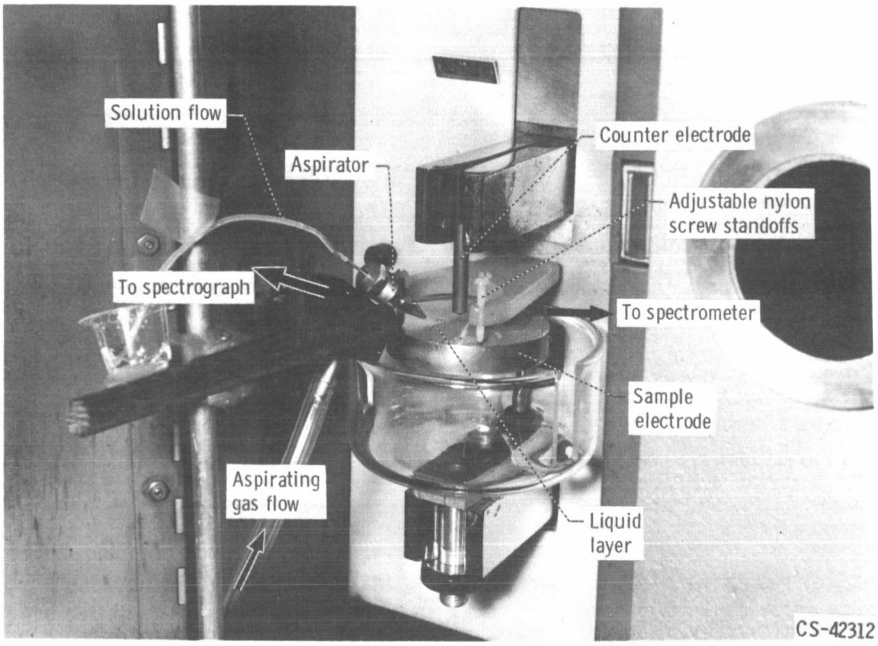

Figure 1. - Apparatus for applying liquid layer on solid samples.

Electrical contact to the sample is made through the spring. The upper portion of the holder is constructed of chemically resistant plastic. Unlike conventional solid sample holders (Petry Stands), this holder permits unhindered solution flow on the electrode surface as well as an uninterrupted view in two directions of the spark emission.

Materials

Aluminum alloy standards were prepared commercially, and tungsten alloy samples were prepared at Lewis. Reference solutions were prepared by dissolving gallium (99.99 percent) in hydrochloric acid, and thallium chloride in distilled water.

RESULTS AND DISCUSSION

Improvement in Analysis

Aluminum standards were sparked under identical conditions with and without the application of a liquid layer to compare the differences in analytical results. Although emission intensity ratios for numerous constituents of the alloys were compiled, only those for silicon will be presented for demonstration.

The comparison of analytical curves, in which the silicon to aluminum line emission ratio was plotted against the concentration of silicon, is illustrated in figure 2 for the

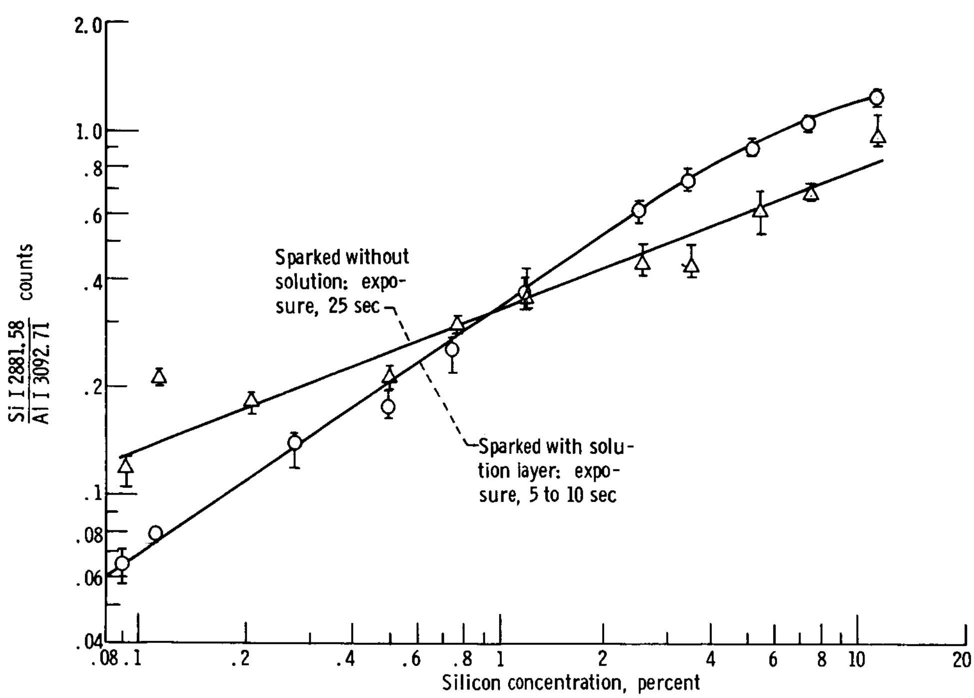

Figure 2. - Analytical curves for silicon to aluminum ratios for sparking under identical conditions with and without solution layer.

determination of silicon in aluminum with and without a gallium solution layer. The slope of these curves, which is directly related to the sensitivity of the determination, increased with the application of the gallium solution layer. The increase in slope in this example was 76 percent. Each point is an average of at least four determinations, and the range of intensity ratio is indicated by a vertical line. The average relative standard deviation of the count ratios is 8.0 percent with the gallium layer, but 9.4 percent without the layer. Further investigation indicated that the relative standard deviation was significantly improved by replacing the Al I 3092.71 line by the Al I 2567.99 line. The Al I 3092.71 line is a strong resonance line, which was observed photographically to be strongly self reversed when used with the liquid-layer solid-sample spark technique. When the Al I 2567.99 line is used, typical relative standard deviations for two standards for 10 or 11 replicate runs averaged 2.8 percent with the gallium layer and 3.7 percent without the layer. These and other comparisons of count precision with and without a liquid layer made during these investigations indicated that determinations made with the liquid layer tend to be more precise than those without the application of the liquid layer. The scatter of values for individual standards around the average analytical curves in figure 2 was decreased when a liquid layer was applied. The increased analytical curve slope improved the concentration precision, and the reduced scatter of points increased concentration accuracy compared with the conventional point-to-plane analysis.

The reduction of exposure time required for a determination was another analytical advantage derived from the application of a liquid layer. The analytical curve obtained with a liquid layer applied required from one-third to one-fifth the exposure required for the curve without the liquid layer to give similar silicon light intensity levels. The application of the liquid layer increased the line-to-background ratio of analytical lines to make this exposure time reduction possible.

Use of Reference Standards

Elements other than those contained in the solid electrode sample were also used as internal standards in analytical determinations. The solute from a solution layer, when used as an internal standard, is referred to as the reference standard. Gallium chloride and thallium chloride solutions were tested as reference standards in this investigation, although indium was used for previous aluminum analysis (ref. 2). Photographic detection was employed to determine line interferences and concentration levels required. Although thallium and gallium were both acceptable for use as reference standards, all photometric determinations were made with gallium solutions.

Similar analytical curves were obtained for aluminum sample constituents, including silicon (0.09 to 11.16 percent), copper (0.03 to 5.17 percent), and iron (0.15 to 2.45 percent), when either an aluminum internal standard or a gallium reference standard was used. This similarity is shown for silicon in figure 3. Four or more determinations were used to obtain the average points plotted. The relative standard deviation of count ratios is 8.0 percent for the silicon-to-aluminum ratios and 5.1 percent for the silicon-to-gallium ratios.

These results indicated that the gallium solute could serve as the reference standard in analysis of aluminum alloys in place of the aluminum internal standard, and corrections for changing aluminum concentrations in different alloys can be avoided.

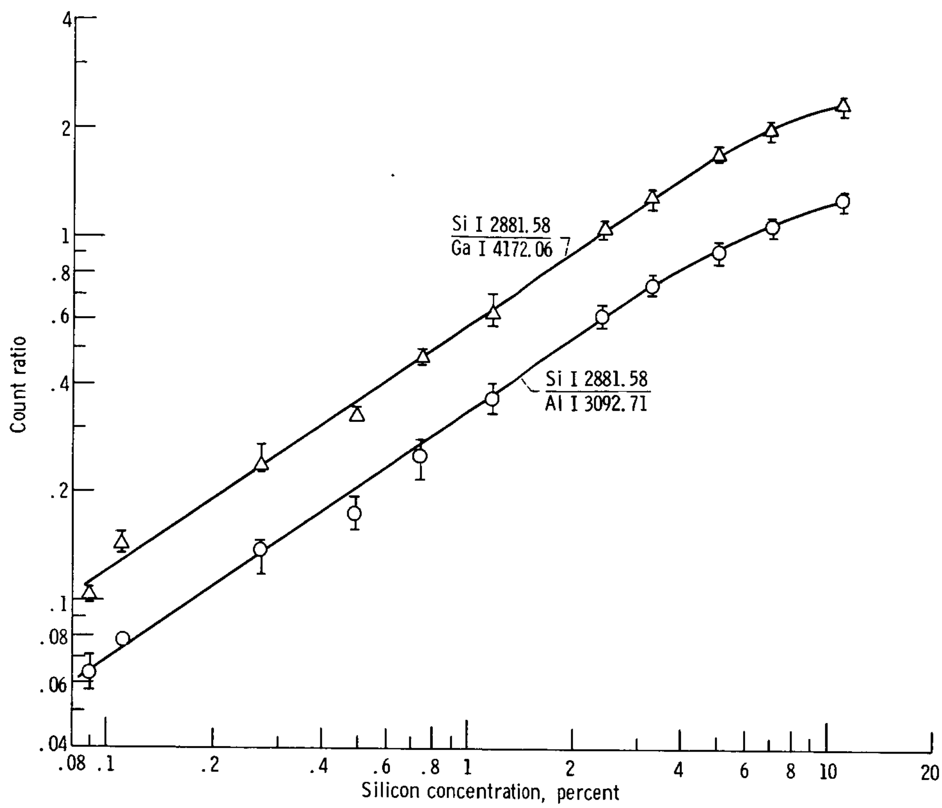

Figure 3. - Silicon in aluminum analytical curves with aluminum and gallium reference lines with gallium solution layer applied.

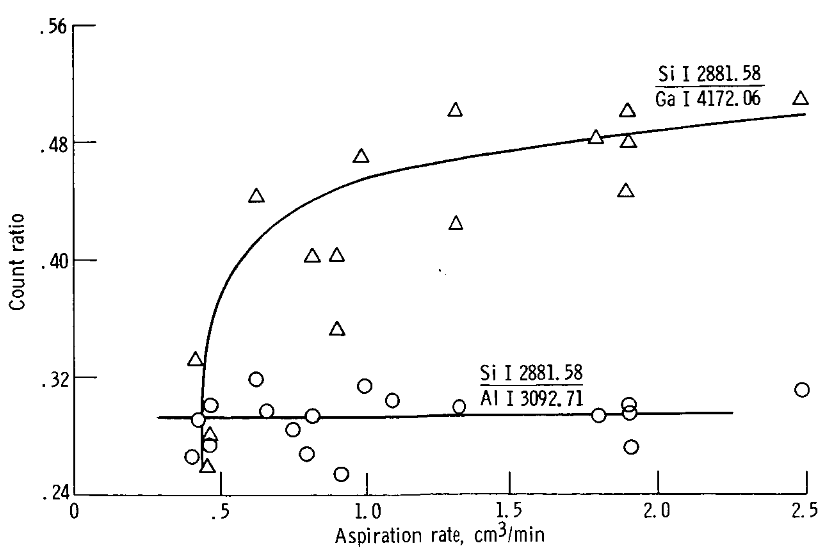

Figure 4. - Effect of aspiration rate on silicon to aluminum and silicon to gallium counts.

Effect of Aspiration Rate

The influence of aspiration rate of gallium solutions on the count ratio of silicon from an aluminum standard containing 0.76 percent silicon is shown in figure 4. The silicon-to-aluminum ratio did not appear to change with aspiration rate. The relative standard deviation of the ratio in figure 4 for which data were collected on two separate days is 6.6 percent. Similar ratios were obtained when water was aspirated. The silicon-to-aluminum ratio was insensitive to the aspiration rate with either water or gallium solution layers. This result was expected for there was no prior indication of the appearance of preferential sampling with the liquid-layer solid-sample spark technique.

On the other hand, the silicon-to-gallium count ratio did respond to the aspiration rate of gallium solution (see fig. 4). The silicon-to-gallium ratio showed insensitivity similar to the silicon-to-aluminum ratio only above a critical aspiration rate of approximately 1 cubic centimeter per minute. To demonstrate the importance of maintaining an aspiration rate in excess of the critical rate, the relative standard deviations of silicon-to-gallium ratios over the range of 0.9 to 2.48 cubic centimeters per minute was compared with the range of 1.0 to 2.48 cubic centimeters per minute. A reduction from 10.6 to 6.0 percent was observed. This improvement in precision illustrated the necessity of using aspiration rates greater than 1 cubic centimeter per minute. Above this critical rate, precision similar to that obtained for the silicon-to-aluminum ratio was, therefore, obtained with the gallium-to-aluminum ratio.

Below an aspiration rate of 1 cubic centimeter per minute, the silicon-to-gallium ratio drops sharply. The source of this drop was not the result of increased silicon counts, but, instead, decreased gallium counts. At low aspiration rates, the gallium count was high, decreasing continuously as the critical aspiration rate was approached and, thereby, increasing the silicon-to-gallium ratio. This effect may result from the variation in gallium layer thickness. At low aspiration rates, the layer thickness is greater and more gallium is present on the sample electrode, which results in high gallium counts. As the aspiration rate increases, the liquid layer is spread thinner until it reaches an equilibrium value at which the silicon-to-gallium counts stablize. The thickness of the layer may be related to the particular atomizer design and may vary with different apparatus. However, once a stable intensity ratio is determined as in figure 4 and the aspiration rate maintained above the critical rate, the use of a reference standard for spectrochemical analysis can be effective.

As the rate of aspiration increases, the amount of material removed from the electrode surface increases. Figure 5 shows the effect with both a water layer and a gallium solution layer. The magnitude and slope of the upper curve, resulting from the gallium layer, is partially explained by observed dissolution of the aluminum alloy by the gallium

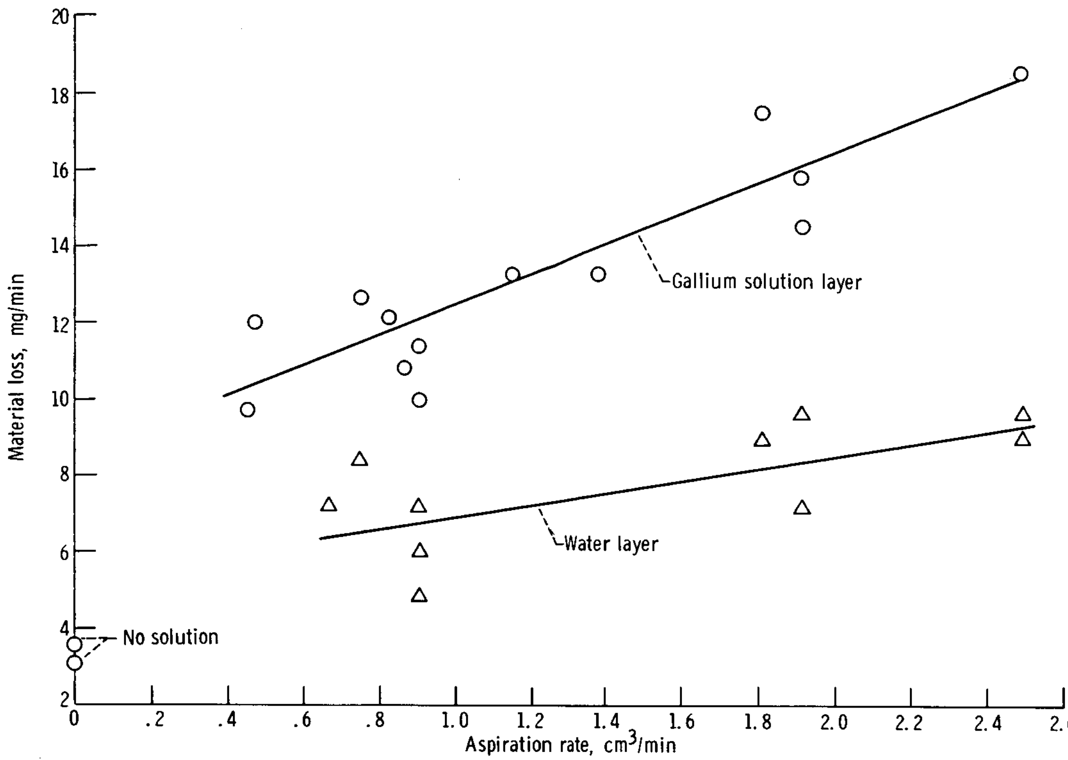

Figure 5. - Comparison of aluminum lost with gallium and water layers at different aspiration rates.

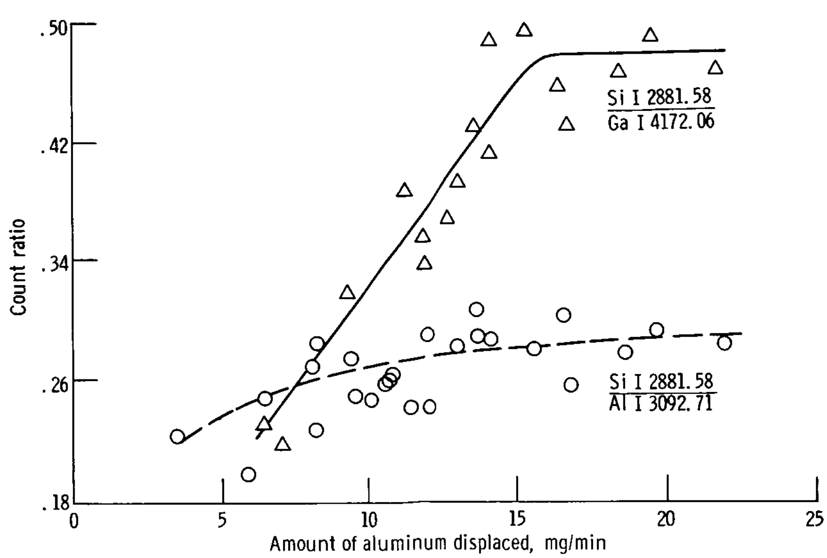

Figure 6. - Comparison of amount of aluminum alloy displaced with silicon-to-aluminum and silicon-to-gallium counts.

acid solution. At 0.45 cubic centimeter per minute, the application of the solution without sparking removed 1.8 milligram per minute of the alloy in the same time sparking would normally occur. Further studies should determine the influence of acid concentration on the rate of sample removal. However, the analytical count ratios should not change if the sample is completely dissolved in proportion to the concentration of the constituents, because they were as effectively sampled from solution as they were from the solid.

Figure 6 demonstrates the relation between the amount of material displaced and the count ratio observed. For a wide range the silicon-to-aluminum ratio remains unaffected, and the silicon-to-gallium ratio shows the dependence on a critical level for relatively constant ratios.

Effect of Spark Inductance

The general applicability of the liquid-layer solid-sample spark technique at various sparking conditions had not been quantitatively studied previously, although visual observation of sparked areas qualitatively showed similar sampling effects, which differed only in magnitude. A quantitative study was made using a fixed capacitance but a variable inductance, which permits the number of discharges per cycle to be maintained without further experimental operating adjustments. The average radio frequency current was directly related to the spark inductance, and the observed sampling and intensity changes were normalized by plotting them against the current and inductance.

Figure 7 shows the amount of change in emission intensities and weight of aluminum displaced with and without the application of a solution layer. The lower curve indicates that, as the inductance becomes smaller (i.e., current becomes larger), the weight of aluminum removed increases. The liquid layer application provided a more effective method of sampling. Although the Al I counts increased with reduced inductance, the increase in Al I intensity was not proportional to the inductance in the same manner as the change in weight of the aluminum actually displaced. For any value of inductance, the change in intensity is always greater than the change in weight. This indicated an influence on the emission of sampled material beyond the increase in material sampled.

Two different, although related, effects may account for this disproportionate increase in line-to-background ratios: The reduction of background emission from atmospheric ions and counter electrode material, and an increase in neutral atom population. The interaction of decomposition products from the solution layer with the atmospheric ions is similar to the interactions observed in previous studies of optical emission analysis methods using solutions (ref. 2). The water is decomposed to atomic hydrogen which interacts with excited states of singly ionized nitrogen and oxygen to produce

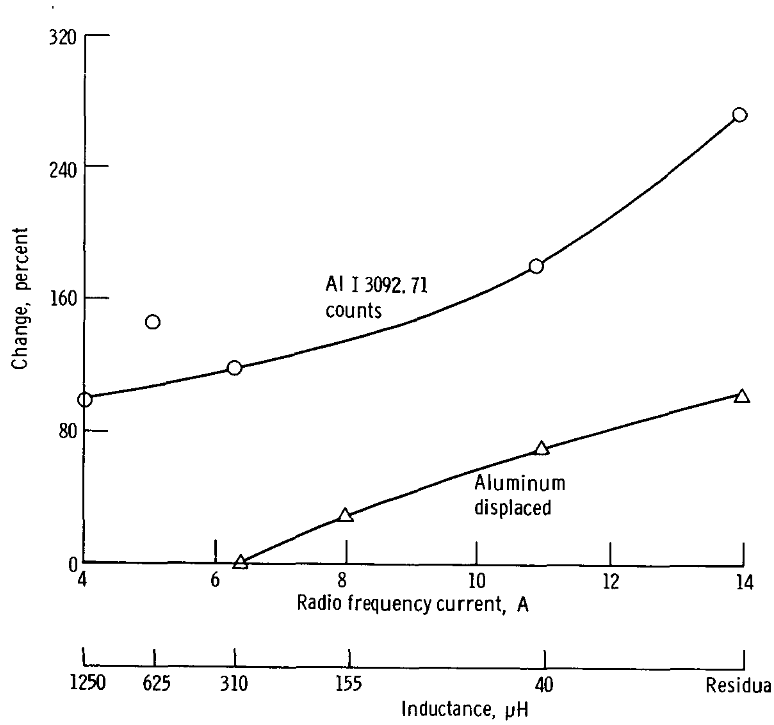

Figure 7. - Comparison between increase in aluminum alloy displaced and aluminum singlet emission with liquid layer as function of spark inductance and current.

the unexcited states. This significantly reduced the emission of these ions in both time-resolved and time-integrated emission spectra. In the present investigations, a similar reduction of ion emission was photographically observed. Emission from carbon neutral atom and ions was also reduced, because with the increase in the amount of sample removed, more sample deposits on the counter electrode. The spark then samples the deposit in place of the counter electrode materials. Both effects decrease emission from sources which may contribute to background. The increase in neutral atom emitting population is greater than the increase in ion emitting population for aluminum when a liquid layer is applied. The mechanism for this observation is not yet clear.

Counter Electrode Deposits and Analysis

The sample electrode material transferred in the spark to the counter electrode was analyzed in the arc. The application of a liquid layer during sparking increased the amount of deposit on the counter electrode, and the solute transported from the solution layer was deposited simultaneously with the material from the sample electrode. These counter electrodes were used for the analysis of the deposited sample. Gallium from the solution layer and aluminum were compared as internal standards. The arc analytical

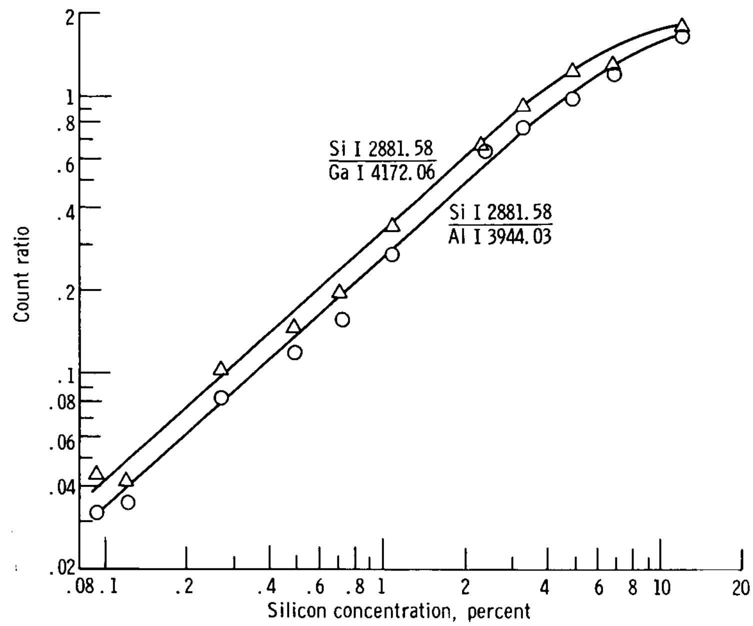

Figure 8. - Analytical curves for silicon from dc arc analysis of counter electrodes with sparked aluminum alloys with gallium solution layer. dc arc, 9.8 amperes; exposure, 33 seconds; argon-to-oxygen ratio, 30; Stallwood jet.

curves for silicon are shown in figure 8. The curves using either aluminum or gallium internal standards have almost identical shape, indicating the lack of discrimination between aluminum and gallium. A similar slope was obtained when the deposit was formed with a water layer on the aluminum sample. Counter electrode deposits, therefore, quantitatively represented the sample constituent concentrations.

The average relative standard deviation of a minimum of four determinations for each of the 11 samples was 24 percent for the silicon-to-aluminum and 21 percent for the silicon-to-gallium ratios. The highest standard deviation was observed for samples collected during the shortest sparking periods.

X-ray diffraction analysis of the counter electrode deposits indicated that the electrode material deposited by pyrolytic processes was similar to those occurring in the formation of flake graphite. For aluminum samples sparked with a water layer applied, gamma alumina was observed, and beta quartz was observed for aluminum alloys with high silicon concentrations. Beta thallium, gallium, copper, and silver were observed in preliminary x-ray analysis for solution layers of thallium, gallium, and copper chlorides and of silver nitrate. These crystalline forms may indicate the thermal history of the vapor or the deposit. For example, gamma alumina can exist to approximately 850° C and is formed between 450° and 620° C (ref. 4). The alpha-beta transition of quartz is 573° C. The absence of other forms indicates that vapor or deposits on the counter electrode may experience thermal temperatures above 573° C but less than 800° C.

Preliminary Tests on Tungsten Alloys

Tungsten alloys containing varying proportions of niobium and tantalum were tested with the application of a water layer during a 60-second exposure. A 48 percent increase in the weight of material removed indicated that further work using this technique may show improvements similar to those observed with aluminum.

CONCLUDING REMARKS

Conventional point-to-plane spark analysis of aluminum alloys was improved when the liquid-layer solid-sample spark technique was employed. Preliminary results indicated that similar improvements may be expected for the investigation of refractory and superalloys, which are difficult to analyze.

For the aluminum alloys studied, material sampling and line emission is increased when a liquid layer is applied to the electrode surface for all values of spark inductance, including those at very low spark current. For the test conditions used for analysis, the increase in slope of silicon analytical curves and the improvement of count precision obtained with the application of a liquid layer combined with higher observed intensities to give substantial gains in analytical measurements with the liquid-layer solid-sample spark technique. For example, the increase in slope was 76 percent and relative standard deviations for repeated determinations were about 3 percent. The increased analytical curve slope and the reduced scatter of values for individual standards increased concentration precision compared with conventional point-to-plane analysis. The application of the liquid layer increased line-to-background ratios of analytically used lines to provide for a one-third to one-fifth reduction in exposure time.

By replacing the matrix element as the internal standard with a reference standard of constant concentration from the solution layer, the determination of elements in widely different base alloys or in differing alloy compositions of the same base material is simplified.

Although the silicon-to-aluminum ratio was insensitive to the aspiration rate of either water or gallium solution layers, the silicon-to-gallium ratio responded to the aspiration rate of gallium solution. Above a critical aspiration rate of approximately 1 cubic centimeter per minute, silicon-to-gallium ratios showed a similar insensitivity. Once a stable intensity ratio is determined and the aspiration rate maintained above the critical rate, the use of a reference standard for spectrochemical analysis can be effective.

An increase in sampling was observed for tungsten alloys which indicated that results similar to those obtained with aluminum may be expected for the analysis of refractory alloys using the liquid-layer solid-sample spark technique. The use of an electrode material transfer technique in the spark combined with increased sampling with an applied liquid layer may prove valuable in the preparation of refractory alloys for arc analysis.

The investigation indicated that previous observations (ref. 2) leading to the development of the technique were supported and that the liquid-layer solid-sample spark method can be applied readily and reliably to conventional high-voltage spark analysis with direct spectrometric readout systems.

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