

THE SPEX SPEAKER

Vol. I—No. 1

January, 1956

Published by SPEX INDUSTRIES, INC.

80-56 230th Street, Queens Village 27, N. Y.

As technology becomes increasingly complex, new fields spring up. Once but branches of the tree, they develop into trees themselves. With this growth comes the broadening of the art and science so that more and more is accomplished with less and less effort. Investigators in the field need media in which to disclose their major advances, and the scientific publications carry this burden. But they also like the opportunity to chat—to discuss minor problems and their solution, to learn how others have saved a minute here and there, to find out what goes on at other labs.

We want the "Spex Speaker" to serve this need. We want to aid our fellow spectrographers in their day-to-day tasks through hints, advice and suggestions. In doing this, we expect often to be controversial: hints are usually seasoned with many ifs, ands and buts.

With our sights so set, we shall appreciate your help. Jot down your solution to a vexing problem and we shall be glad to print it over your name. Likewise, if you disagree with what we say, get into the act. When you have a question you want answered, we'll print it and hope that one of our other readers will supply the answer.

Now, we don't know whether this newsletter is a monthly, quarterly, annual or even a once-only. Won't you help us make that decision?

SPECTROCHEMICAL ANALYSIS FOR TRACE ELEMENTS

I. When Sample Size is Unlimited

By A. J. MITTELDORF

Introduction

In trace-element analysis, the major problem confronting the spectrographer is how he can obtain the maximum sensitivity with his instrumentation. He strives to record spectral lines of elements, the total weight of which may be as little as 0.01 gamma. And neither are his efforts of academic interest alone. For trace-element problems are important in metallurgy where 0.0005% of boron will improve the hardenability of steel; in agriculture where a few ppm of cobalt in the soil are vital to the health of grazing animals; in electronics where the performance of a transistor is poisoned by the presence of less than 1 ppm of many elements; in phosphor manufacture where a trace of copper activates zinc sulfide; in geology where the presence of minute concentrations of elements in rivers guides scientists to deposits of those elements; in semi-quantitative spectrochemical analysis where the sample is diluted so that its constituents are reduced to traces.

The examples given have one point in common: the sample is large or unlimited in size. But, equally important are problems involving a few mg or less of a sample. The composition of the deposit on an electrical contact may reveal the reason for the failure of that contact. The analysis of a microscopic inclusion may disclose the source of the inclusion.

To the spectrographer, the problems of the unlimited and limited sample have points in common. But they also differ considerably. The latter is one in which speed and sensitivity are closely akin. There is so little sample that its spectrum must be recorded before it vanishes from the electrode. In analyzing samples of unlimited size, on the other hand, speed is of little concern. The

spectrographer can always use more sample and superimpose spectra if further registry of spectral lines is needed.

In this article, we shall discuss the unlimited sample problem; in a subsequent article, the limited sample.

Spectrograph

With the unlimited sample on hand, the first question is which spectrograph to use if more than one is available; how to use the spectrograph if but one is in the laboratory. Here the primary consideration is dispersion. Many investigators have shown that sensitivity is directly related to dispersion. The sensitivity of any measurement corresponds to a signal-to-noise ratio. Translated into spectrographic terms, sensitivity is a line-to-background ratio. In an instrument of low dispersion, the background behind a line is concentrated. In one with large dispersion, the same background is spread out over a large area. The line itself in both spectrographs, being an image of the slit, remains the same width. Greater dispersion is thus responsible for lowered background, a greater signal-to-noise ratio and, in turn, better sensitivity.

In "Practical Spectroscopy,"¹ Harrison, Lord and Loofbourrow cite a beautiful example of how dispersion and sensitivity are so intimately related. Using a 35-ft. spectrograph, ten tin lines could be photographed in a certain sample. With a medium quartz instrument, no tin lines appeared from the same sample, regardless of the exposure time.

In general, anything that improves the *effective* dispersion of a spectrograph will improve sensitivity. A grating spectrograph, for example, should be used at its highest useful order. Of course, *effective* dispersion should be emphasized. In the new Ebert

spectrographs, it is possible to utilize the 14th and even higher orders. Because of optical aberrations, pressure broadening of lines and many other factors, no gain in sensitivity will be noted beyond perhaps the 4th or 5th orders. With a prism instrument, it will often be found that a line in the short (high dispersion) wavelength region will be more sensitive than one at a longer wavelength, despite the handbook listings to the contrary.

Resolution is another important consideration in achieving optimum sensitivity. A weak, well-resolved line may just appear above its background while one poorly resolved will dissolve into the background. Basically, illumination is the factor to contend with here. There is a direct relationship among illumination, resolution and sensitivity. Maximum resolution of any optical instrument is attained when its optics are just filled with light. Applied to a spectrograph, the illuminating system which just fills the grating or prism will result in the best resolution. External optics are so arranged that an image of the source is obtained on the entire height of the grating or prism collimator.

Now resolution is a horizontal affair, involving the width but not the length of a line. Its vertical counterpart is astigmatism or, rather, the lack of astigmatism. Just as a poorly resolved line is spread out horizontally, so an astigmatic line is spread out vertically. The effect is the same: a sacrifice of line intensity and consequent loss of sensitivity. Many grating and most prism spectrographs are stigmatic over wide wavelength intervals and so the effect does not apply to them. With instruments that suffer from astigmatism, it is possible to so set the external optics that there is a limited wavelength region where the images are stigmatic. These settings should be made for the region of interest.

While on the subject of the slit, the question is often asked, what is the optimum slit width for the highest signal-to-noise ratio? The intensity of a spectral line will increase to a limiting value as the slit width is increased. But the background increases at a more rapid rate. Accordingly, it is wise to use the finest slit width to obtain the highest line-to-background ratio. In reducing the slit width, however, a point is reached beyond which other gremlins enter the picture. In a grating instrument, for example, satellites may begin to appear at very narrow slits. In a prism instrument, the slit should be kept as fine as possible without introducing certain diffraction effects.

Earlier, we spoke of illumination in terms of the resolution of the spectrograph. Equally important is illumination so adjusted that the spectral lines are transmitted but all extraneous light is removed. For example, light from the incandescent electrodes should not be permitted to register on the plate. The best way of accomplishing this is to use a system of illumination whereby the electrodes are focussed on an aperture on the optical bench. A hole then becomes the apparent source, the images of the electrodes blocked out before the slit by the aperture jaws. Another way of doing this is to focus the light on an aperture at the grating or prism. This, however, allows unwanted light into the spectrograph, some of which may be scattered and terminate in unwanted background.

C. The Source

With some notable exceptions, it has been found that the dc arc yields the best overall concentrational sensitivity. This seems to be related to the temperature to which the element is raised in the source. For example, at relatively low flame temperatures, the sensitivity of sodium is poorer than it is at higher arc temperatures. Vallee,² however, recently reported on the sensitivity

of sodium in a high temperature flame, that was produced by burning cyanogen. In this source, the sensitivity of sodium was as high or higher than that in a conventional arc. Theoretically, an optimum temperature for achieving the greatest sensitivity for a particular element should be possible. This is a temperature just lower than that necessary to produce transitions other than those resulting in "persistent" lines. In other words, if all of the energy is expended by the production of a single spectral line, that line will be strong. If, on the other hand, more energy is provided, the element will produce lines in addition to the persistent lines and at their expense.

This may be at least a partial explanation of the "cathode layer" effect. Used extensively in Europe today, this source has been shown by Strock³ and others to be more sensitive than the conventional dc arc more commonly used in this country. In the cathode layer technique, the sample is made electrically negative. In addition, a very small sample (about 15 mg) is used and the electrode is very narrow ($\frac{1}{8}$ ") with a crater drilled in it to a depth of perhaps $\frac{3}{8}$ ". The arc gap is usually about 10 mm. By contrast, the more common dc arc excitation uses a $\frac{1}{4}$ " diameter electrode drilled to a depth of $\frac{3}{16}$ ", the sample is made positive and the gap is but 2-3 mm. A photograph of the profile of the arc column of a cathode layer burning reveals that the lines of a good many of the elements are considerably stronger at the cooler cathode. They taper off towards the anode. In addition, the line-to-background ratio is stronger at the cathode. No full explanation of the phenomenon has been offered. But part of the explanation may be that the temperature near the cathode is close to the optimum required to produce only the persistent lines of many of the elements. At the higher temperatures near the anode, other lines are excited, reducing the energy emitted by the persistent lines.

Another source of high sensitivity is the carrier distillation technique devised by Scribner and Mullin⁴. It is used for the determination of relatively volatile elements in the presence of refractory ones. A material such as gallium oxide is added to the powder to be analyzed. This sweeps the volatile elements up into the arc to such an extent that, when used originally for the analysis of uranium, lines of uranium were practically non-existent while the impurity lines were prominent.

In still another way, differences in volatility may be taken advantage of to produce the best signal-to-noise ratios for groups of elements. This is through a moving-plate analysis. The sample is burned to completion but every few seconds the plate is racked. By spotting the best time interval for a particular element, further improvement in the sensitivity of that element is achieved.

Under exceptional circumstances, the use of an atmosphere other than air around the source should be considered. Owen⁵ has described a simple container in which electrodes may be flooded with gases such as carbon dioxide or one of the inert gases. These are useful in reducing the cyanogen bands so that elements whose principal lines fall in these bands are detected more readily. They also prevent the formation of oxides whose molecular spectra are usually complex and contribute to the background.

Buffers

A spectrographic buffer is a material which, when mixed with the sample, improves the reproducibility and/or the sensitivity of the analysis. A buffer which enhances sensitivity must, itself, have a high ionization potential and should be reducing rather than oxidizing. Graphite seems to be the best overall choice. Many spectrographers use graphite but, in addition, mix in such materials as lithium carbonate or zinc oxide. These serve to provide an internal standard and, with many materials, provide "smoother" burns to improve precision.

Chemical Treatment

Two types of improvement are made in a sample to be analyzed through appropriate chemical treatment: the elements sought may

Our cupboards are full . . . We now have large stocks of United and National preformed electrodes and rods, Eastman plates and film on hand for IMMEDIATE DELIVERY. Request our Catalog 55F for details. Also, be sure to compare our prices—especially on plates and film.

be concentrated by separation techniques; elements with low ionization potential may be removed.

The importance of concentrating an element is obvious when an unlimited sample is on hand. The spectrographic plate "sees" the total number of atoms of an element. The more that can be placed in an electrode, the better the sensitivity of that element. Of the wide variety of reagents available for separating out trace elements, the organic ones such as dithizone, 8-hydroxyquinoline have been found to be particularly useful. Mitchell⁶ described the use of a mixture of 8-hydroxyquinoline, tannic acid and thionalide which will recover microgram quantities of Co, Ni, Mo, Zn, Sn, Pb, V, Cr, Ag, Au, Ga, Fe and Cu in the presence of excesses of an aluminum carrier.

As stated, such separations have a double purpose. They concentrate in a small volume the elements sought. They also remove the alkalis and other elements of low ionization potential. Such elements, by keeping the ionization potential at the arc low, prevent elements of higher potential from producing spectral lines.

Photographic Emulsion

When an unlimited sample is available, the plate chosen for the analysis need not be a high speed one. In fact, it is generally advisable to use a plate of moderate speed to take advantage of its other superior qualities. A moderate speed plate usually has a fine grain, processes readily, has a low fog level and high contrast.

An emulsion with these characteristics is Spectrum Analysis #1. It has excellent resolution, excellent processing characteristics, a very low fog level and is sensitive over the region 2200-4300A, where most of the lines of the elements appear. On the minus side, it has a variable contrast with wavelength changes and beyond 3600 its contrast is so high that an element can be determined through only a single decade of concentration, e.g. from 0.01 to 0.1%.

The photographic emulsion used will depend on which elements are sought. For example, if arsenic were sought in an organic ash, it would pay to use a fast emulsion such as 103-0. Because it is so volatile, arsenic requires but a short exposure. The alternative would be to superimpose a number of exposures on a slower emulsion such as SA #1.

In trace-element work, it is always desirable to run exposures until the sample is totally consumed. In this fashion, refractory elements will not escape detection. In doing this, however, chances are that many lines will be over-exposed. To accomplish both simultaneously, the use of a step-sector or step-filter is recommended. The exposure for one line will be optimum at one step; for another, at another step.

Conclusions

The overall concentrational sensitivity for any element may be improved ten, one hundred and even a thousand-fold by taking full advantage of the instrumentality available and through the use of techniques such as those briefly described. Each problem must be considered individually and the best combination of conditions employed to achieve the desired results.

A point-by-point Check-List for improving sensitivity is recapped below:

Improving Spectrographic Sensitivity When Sample Size is Unlimited

I. Spectrograph

- A. The instrument should be used at its highest effective dispersion.
- B. If there is a choice of a spectrograph, that with the highest effective dispersion should be chosen.
- C. The instrument should be used at its optimum resolution by 1) filling the dispersing element with light; 2) using as fine a slit as practical.
- D. A stigmatic instrument or one set for the least astigmatism is required.
- E. The incandescent electrode images should be masked out.

II. Source

- A. The dc arc should be employed, generally speaking.
- B. The cathode layer technique should be investigated.
- C. Time-intensity studies should be made to ascertain the optimum exposure time intervals.
- D. For determining volatile elements in the presence of non-volatile ones, the carrier distillation technique is useful.
- E. Under exceptional conditions, an atmosphere other than air will prove helpful.
- F. Replicate exposures are helpful in determining traces of volatile elements.
- G. The sample should always be burned to completion when all of the elements are to be reported.

III. Buffers

- A. The sample should be mixed with a buffer, such as graphite.
- B. A second material is often desired to smooth out the burning and to provide an internal standard.

IV. Chemical Concentration

- A. Organic reagents will serve to remove elements of low ionization potential and at the same time to concentrate elements of interest.
- B. The use of simple concentration techniques such as evaporation, filtration and magnetic separation should not be overlooked.

V. Photography

- A. The emulsion chosen should have a relatively high contrast, be easily processed, not distort on processing, have a low fog level and excellent resolution.
- B. Step-sector or step-filter exposures will permit optimum exposures for a large number of elements simultaneously.

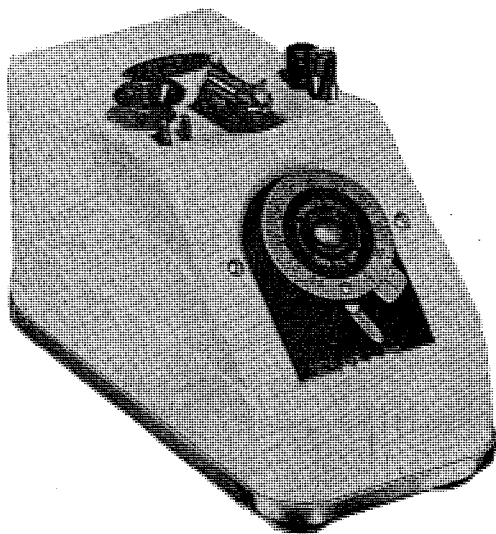
References

- 1 Harrison, G.R., Lord, R.C. and Loofbourow, J.R. "Practical Spectroscopy," Prentice-Hall (1948).
- 2 Vallee, B.L., unpublished paper at Trace Element Symposium held in New York, November, 1955.
- 3 Strock, L. W., "Spectrum Analysis with the Carbon Arc Cathode Layer," Hilger, London (1936).
- 4 Scribner, B.F. and Mullin, H.R., *J. Res. Nat. Bu. Stds.* 37:369 (1946).
- 5 Owen, L.E., *J.O.S.A.*, 41:139 (1951).
- 6 Mitchell, R.L. "The Spectrographic Analysis of Soils, Plants and Related Materials," Commonwealth Bureau of Soil Science, Harpenden, England (1948).

Now available are preformed electrodes cut from National REGULAR-GRADE graphite stock. At a cost of 1/4 that of the high purity preformed electrodes, they will save you money in all applications where trace elements are not of concern. They are machined on automatic screw machines using carbide-tipped tools. There is no contamination, excellent uniformity of dimensions and a price which is lower than that when you do-it-yourself. Sketch the cross-section of the electrodes you are now using on the enclosed postage-free card and we'll send you a quotation promptly.

WIG-L-BUG

The standard dental tool for triturating amalgams, this instrument is particularly useful for mixing sample powders for spectrochemical and x-ray analysis. It consists of a motor controlled by a 0-60 second timer which oscillates a pair of clips. The vial in which the sample is held is mounted in these clips and the motor started. Swung through a $6\frac{1}{2}^\circ$ arc in a figure-8 motion at 3200 rpm, a plexiglas ball inside the vial strikes four blows per cycle against the ends of the vial. In 10 seconds, the normal mixing time, some 2000 blows are thus struck.



As used by the dentist, the amalgam is placed in a reusable cartridge together with a pestle. In laboratories, however, the cartridge becomes contaminated after a single use and is quite difficult to clean. To overcome this, we supply a polystyrene vial in place of the cartridge and a plexiglas ball instead of the pestle. The cap of the vial is of polyethylene so that the entire assembly may be cleaned with mineral acids for trace-element work. The ball, itself, is expendable: its cost is but a penny. Holding about 1 ml of sample, the vial costs 3¢ and is used to retain the unused portion of the sample for reference purposes.

- ★ Mixes all powders regardless of particle size differences, tendency to cake or differences in hardness.
- ★ Simplifies and speeds up mixing powders—10 seconds are sufficient for most samples.
- ★ Stainless steel cartridge and pestle included for mixing organic materials, e.g., for infrared KBr technique.
- ★ Materials are weighed directly into the vial in which they are mixed and then stored.
- ★ Vials, caps and ball-pestles are of plastic and so cannot introduce metallic impurities.
- ★ The assembly is easily cleaned using mineral acids.
- ★ Inexpensive—per sample cost is 4.2¢, less than the cost of many vials, themselves.

3110B	Wig-L-Bug. Operates on 115 volts, 50-60 cy; net weight 8 lbs., complete with vial adapter; black housing	\$55.00
3110W	Wig-L-Bug. Same as above but in a white (ivory)	\$60.00
3111	Vial, for use with Wig-L-Bug; $\frac{1}{2}$ " diameter x 1" long, polystyrene with polyethylene slip-on cap.	
	per 100	\$ 3.80
	per 1000	\$30.00
3112	Ball-pestle, clear plexiglas, $\frac{3}{8}$ " diameter, for use with Wig-L-Bug.	
	per 100	\$ 1.80
	per 1000	\$12.00
3113	Vial Adapter for Wig-L-Bug	each \$3.50

SEND US AN UNMIXED SAMPLE AND WE SHALL RETURN IT AS MIXED IN THE WIG-L-BUG. THE SAMPLE WILL BE RETURNED IN THE PLASTIC VIAL WITH THE PLEXIGLAS BALL DESCRIBED ABOVE.

STAINLESS STEEL SWATCHES

Like our #2000 Wrought Aluminum Swatches, these are used for the rapid identification of a sample. The spectrographer (emission or x-ray) merely matches the unknown with one of the swatches. Although there are, today, a large variety of stainless or corrosion-resistant steels, most of them fall into three categories. Stainlesses in the 300-series are 18-8's (18% Cr, 8% Ni). Widely used in sheet, tubing, etc., they are, however, sometimes subject to intergranular corrosion. This is caused by the presence of residual carbon and resulting carbide precipitation when the metal is worked. To overcome this, steels are stabilized with

titanium (type 321) or tantalum and niobium (type 347). Both of these steels are far less apt to crack under mechanical or thermal stress. Type 347 is commonly specified for welding rods because, unlike the titanium in 321, the niobium and tantalum in 347 do not oxidize when welded properly. Type 316 contains about 2½% molybdenum and is widely used as containers for chemical baths such as photographic solutions. The ferritic stainlesses (400-series) contain chromium but little or no nickel. They are more machinable, far less costly but not as corrosion-resistant as the 300 stainlesses.

2100	Stainless Steel Swatches, on beaded chain, including a certificate giving the nominal composition of each swatch; each is about 4" long x 1" wide and $\frac{1}{8}$ " thick. The set includes the following A.I.S.I. steels: 302, 321, 347, 316, 410	
	Set of Five	\$18.00