

SPEX METHODS FOR SEMI-QUANTITATIVE SPECTROCHEMICAL ANALYSIS

OUR first product was Spex Mix, a material now popular in thousands of laboratories. Much used, and even copied, during the seven intervening years the series of standards developed with Spex Mix as the base, as well as the techniques with which they are applied, have undergone many refinements. In the present review we hope to update original suggested procedures with current information.

Instrumental analytical methods, offering indirect measurements, usually require comparison standards to be run along with an unknown. Because the emission intensity of a particular element is far different in a steel alloy than say an aluminum alloy, the proverbial sample of "gook" defies comparison with any standardized material even for the spectrographer fortunate enough to have accumulated a library-sized assortment of reference materials. Long ago recognized as the "matrix effect," this remains the most significant and economically important problem in spectrochemical analysis. With Spex Standards and a technique of dilution the matrix effect can be conveniently overcome.

If, for example, the G (graphite base) Standards are to be used, the unknown is first diluted with graphite in a ratio of 1:9, and if necessary for high concentrations of elements present, 1:99 and 1:999. The matrix is thus essentially converted to graphite—identical for unknown and standard alike. Seeing mainly graphite and only 10% or less sample, the spectrograph is coaxed into giving reliable answers and the original matrix is essentially by-passed.

To date we have made available ten sets of semi-quantitative reference materials, each containing 49 elements. Our base, Spex Mix, consists of compounds (mostly oxides) of 49 common elements weighed out so that each element is present at exactly the same concentration, 1.28%. That is, from the gravimetric factor, enough silver oxide is weighed out to yield 1.00g of silver; enough antimony oxide weighed out to yield 1.00g of antimony; enough calcium carbonate for 1.00g of calcium, etc. Separately, each compound is first ground down to .325 mesh and, after being weighed, the compounds are ball-milled for many hours to assure uniformity. The number 49, divided by the total weight of the compounds gives the figure of 1.28% concentration for every element present. The actual elements present in Spex Mix are listed below:

| | | | | | | |
|----|----|----|----|----|----|----|
| Ag | Br | Cs | I | Na | Se | Ti |
| Al | Ca | Cu | In | Nb | Si | Tl |
| As | Cd | F | K | Ni | Sn | U |
| B | Ce | Fe | Li | P | Sr | V |
| Ba | Cl | Ga | Mg | Pb | Ta | W |
| Be | Co | Ge | Mn | Rb | Te | Zn |
| Bi | Cr | Hg | Mo | Sb | Th | Zr |

The type Z set utilizes a zinc oxide matrix and is recommended for the analysis of organic ashes. The type L set is similar to the Z set but has a lithium carbonate base and is recommended for the analysis of lubricating oils, crankcase sludges, and other organic residues. Calcium carbonate base standards are useful for the analysis of water deposits. Other standards, used chiefly for special substances, have as bases silicon dioxide, aluminum oxide, calcium carbonate, germanium oxide, gallium oxide, indium oxide, and nickel oxide; these may be mixed in any proportion to simulate the basic composition of the unknown. Still other standards are available on special order.

All of the above standards come in sets of three containing 2 grams each. The standards contain 0.1%, 0.01%, and 0.001% of each of the 49 elements. G standards have a graphite matrix and are recommended for the analysis of inorganic materials. In some applications, they are advantageously blended with equal parts of the L standards in order to obtain a convenient internal standard while maintaining a reducing atmosphere in the arc. This set contains not three, but four standards. Three are as described for the other standards; the fourth contains 0.0001% of each of the elements. The actual graphite chosen is National Carbon Company SP-2X (-100 mesh). The coarse particles in this material have relatively little tendency to fly out of the electrode cup during a burning, a factor often overlooked when poor precision is a problem. Other related materials available include: (1) a complete catalogue of highest purity materials suitable for use as buffers, diluents, and matrices for spectrochemical and other uses, including base materials for all of the listed standards; (2) an "Element Kit" containing 2g quantities of compounds of the 49 elements present in the standards; (3) a R. U. type of powder named "Qual Mix" containing most of the elements present in the semi-quantitative standards, but blended so that only a few prominent lines of each element appear when the material is burned in a dc arc as directed; (4) a "Qual-Mix Atlas" of 20 spectral charts, prepared with a large grating spectrograph, has intense lines of elements marked and identified; (5) "Noble Metal" and (6) "Rare Earth" standards are also available. These are sold in sets similar to the standards mentioned previously; instructions for their use are given below.

Let us proceed to analyze, hypothetically, an unknown powder, using G standards. We take 10 mg of the sample and mix it with 90 mg of graphite to obtain a 1:10 dilution. To determine elements above 1%, a second ten-fold dilution is required and a third for elements above 10%. A Mixer/Mill or Wig-L-Bug with a plastic ball and vial is suggested for the dilution operations. The shortest mixing time possible, usually

10-60 seconds, is desirable in order to keep the grinding action to a minimum.

We prepare four samples which we shall refer to as follows:

- X the original unknown
- .X the original unknown diluted with graphite 1:9
- .OX the original unknown diluted with graphite 1:99
- .OOX the original unknown diluted with graphite 1:999

The actual technique recommended depends on the accuracy requirements. In a typical procedure, all of these materials are burned to completion on the same plate and under the same conditions as the entire set of G standards. A dc arc of 5-10 amperes is employed; the sample electrode is made electrically positive. Typical electrodes used for this work are an undercut L-3906 (Spex 4004), or a narrow (1/8") diameter electrode, L-3979 (Spex 4020), to minimize arc wandering. Whatever the electrode used, the sample must be burned to completion.

Table I is a hypothetical example of the kind of results to be expected. Here it was not necessary to dilute the sample to .OOX since it was known beforehand that all elements were present below 10% concentration.

TABLE I

Hypothetical Example of Analysis Using G Standards

| Material | Relative Intensity (0 is not detected, 7 is very strong) | | | |
|----------|---|----------|----------|---------|
| | Si 2881A | CU 3247A | Ag 3281A | B 2498A |
| X | 7 | 2 | 0 | 0 |
| .X | 6 | 1 | 1 | 0 |
| .OX | 4 | 0 | 0 | 0 |
| G-1 | 4 | 4 | 4 | 4 |
| G-2 | 3 | 3 | 3 | 3 |
| G-3 | 2 | 2 | 2 | 2 |
| G-4 | 1 | 1 | 1 | 1 |

Interpretation of this table would be as follows: the silicon at the 100 times dilution (.OX) matches the silicon in G-1. In other words, it contains approximately .1% at this dilution. Multiplying by the dilution factor of 100, the sample is thus estimated to contain about 10% silicon. The copper in this sample at the .X dilution matches G-4 and, therefore, represents about .000X%. Multiplying by the dilution factor, the original sample contains about .00X%. The silver presents an interesting example in that it is not detected in the original sample but detected at the first dilution. This frequently occurs, the graphite diluent actually tending to improve sensitivity. In this example, the silver concentration is around .001% in the original sample. Boron is not detected in the sample nor in any of its graphite dilutions. Without standards, it would be ambiguously reported "not detected." One big advantage of the Spex method is that the determination is amplified to read "not detected, less than .001%." We reason thus: since boron shows in all four of the standards, its limit of detection is at least .0001%. This means that .0001% would be detected in .X, the first dilution of the sample. Multiplying by 10, as previously, we conclude that the boron content of the original sample, if present, is less than .001%.

ORGANIC compounds fall into another category mainly because of the necessity of ashing them before analysis. Pros and cons to both, either wet ashing or dry ashing may be

employed. In general, there is a tendency to add impurities in the former and lose impurities in the latter.

A typical dry ashing procedure for the analysis of organic materials would be to start with a one gram sample of the material and then char it in a platinum crucible. The time and temperature depend on the particular material but both should be kept to a minimum. After charring, 0.10g of spectrographic grade zinc oxide or lithium carbonate is added and mixed in the crucible for about a minute with a small spatula. The mixture is then ashed at about 450° C and ground to a homogeneous powder. Since this material is to be analyzed against the Spex Z (zinc oxide) or L (lithium carbonate) standards, a small amount of each of the standards can be ashed as "blanks". In other words, an element such as arsenic will volatilize similarly in the standards and the unknown so that a correction factor will be automatically applied in this manner. A word of caution should be given here. Do not add zinc oxide directly to the organic material before it is charred. Partial reduction of the zinc oxide to the base metal may occur with consequent loss of accuracy. The procedure given above concentrates the elements in the organic material by a factor of ten. Of course, if one starts with 10g or 100g of the original material, a concentration of 100 or even 1000 is possible. In the final calculations, values are, of course, multiplied by the appropriate factor.

SPECIFICALLY prepared Rare Earth Spex Mix (RESM) and Rare Earth L (REL) Standards are used for the determination of rare earth elements in samples. RESM and the REL standards contain Ce, Dy, Er, Eu, Gd, Ho, La, Lu, Nd, Pr, Sc, Sm, Tb, Tm, Y and Yb. RESM contains 5.28% of each of the elements and, like the common element Spex Mix, RESM is used for the analysis of relatively pure substances (a method to be described later). The four REL Standards are dilutions of RESM with spectrographic grade lithium carbonate containing 0.50%, 0.050%, 0.0050%, and 0.00050% of the above sixteen elements. The REL standards are used for the semi-quantitative determination of rare earth elements in mixtures. The Rare Earth Element Kit contains individual vials of each of the elements as oxides. These are used for identifying lines of rare earths, the spectra of which are quite complex. They are also useful for preparing individual standards for specific purposes. To analyze an unknown, it is diluted with spectrographic grade lithium carbonate by successive factors of 10, and the procedure described for our common element standards is followed.

Noble Metal Spex Mix (NMSM) and Noble Metal G (NMG) Standards contain Au, Ga, Hf, In, Ir, Pd, Pt, Re, Rh, Ru. The NMSM contains 9.32% of each of these ten elements. The NMG Standards are dilutions of NMSM with spectroscopic grade graphite powder, containing 0.50%, 0.050%, 0.0050%, 0.00050%, of each of the 10 elements above. Again an unknown is analyzed after dilution with graphite by successive factors of 10. A chart of detection limits we have noted is given below. Although other lines may be cited for many of the elements, the lines in Table 2 were selected because of freedom from interference by line or band spectra.

Analyses were made with our 3.4-meter Ebert mount spectrograph. A dc arc discharge of 7 amperes and a water-cooled Stallwood Jet was used with a 30% oxygen, 70% argon mixture at a flow rate of 5 lpm. The samples were packed in shallow crater electrodes (Spex 4004) and burned to completion. A three-lens optical system reduced scattered light. These values, subject to immense instrumental variables, cannot be guaranteed for other laboratories.

TABLE 2
COMPARISON OF SENSITIVITY

| Element | Line, A | Limit of Detection, ppm | | Element | Line, A | Limit of Detection, ppm | |
|---------|---------|-------------------------|---------------|------------------------|---------|-------------------------|---------------|
| | | Open Arc | Stallwood Jet | | | Open Arc | Stallwood Jet |
| Ag | 3280.7 | 1 | .5 | RARE EARTH L STANDARDS | | | |
| Al | 3092.7 | 10 | 5 | Ce | 4186.6 | 10 | 5 |
| As | 2349.8 | 100 | 50 | Dy | 4046.0 | 5 | 2 |
| B | 2497.7 | 2 | 2 | Er | 3692.6 | 5 | 2 |
| Ba | 4554.0 | 5 | 2 | Eu | 4594.0 | 5 | 2 |
| Be | 2348.6 | .1 | .5 | Gd | 3422.5 | 10 | 2 |
| | 3130.4 | .5 | .02 | Ho | 3891.0 | 5 | 2 |
| Bi | 3067.7 | 5 | 2 | La | 3949.1 | 5 | 2 |
| Ca | 4226.7 | 1 | .2 | Lu | 2615.4 | 5 | 2 |
| Cd | 3261.1 | 20 | 10 | Nd | 4303.6 | 20 | 5 |
| Ce | 4186.6 | 1000 | 500 | Pr | 4225.3 | 20 | 5 |
| Co | 3453.5 | 20 | 5 | Sm | 4424.3 | 20 | 5 |
| Cr | 2835.6 | 10 | 5 | Sc | 4023.7 | 1 | .5 |
| Cs | 4555.4 | 500 | 500 | Tb | 3509.2 | 50 | 10 |
| Cu | 3247.5 | 1 | .5 | Tm | 3462.2 | 5 | 2 |
| Fe | 3020.6 | 5 | 2 | Y | 3242.3 | 5 | 2 |
| Ga | 4172.1 | 20 | 5 | Yb | 3289.4 | 1 | .5 |
| Ge | 2651.2 | 5 | 5 | | | | |
| Hg | 2536.5 | 500 | 50 | | | | |
| In | 4101.8 | 20 | 5 | | | | |
| K | 4044.1 | >1000 | 1000 | | | | |
| Li | 3232.6 | 500 | 500 | | | | |
| Mg | 2795.5 | .2 | .2 | | | | |
| Mn | 2576.1 | 5 | 1 | | | | |
| Na | 3302.3 | 500 | 500 | | | | |
| Nb | 3094.2 | 10 | 5 | | | | |
| Ni | 3414.8 | 20 | 5 | | | | |
| P | 2535.7 | 100 | 50 | | | | |
| Pb | 2833.0 | 20 | 5 | | | | |
| Rb | 4201.8 | >1000 | 1000 | | | | |
| Sb | 2598.0 | 50 | 50 | | | | |
| Se | 2062.8 | 1000 | 500 | | | | |
| Si | 2881.6 | 1 | .5 | | | | |
| Sn | 3175.0 | 20 | 5 | | | | |
| Sr | 4077.7 | 50 | 5 | | | | |
| Ta | 3311.2 | — | — | | | | |
| Te | 2385.8 | 500 | 100 | | | | |
| Th | 4019.1 | 500 | 500 | | | | |
| Ti | 3349.0 | 10 | 1 | | | | |
| Tl | 3775.7 | 50 | 20 | | | | |
| U | 4241.7 | 500 | 500 | | | | |
| V | 3093.1 | 20 | 5 | | | | |
| W | 4302.1 | 100 | 100 | | | | |
| Zn | 3302.6 | 50 | 10 | | | | |
| Zr | 3496.2 | 50 | 10 | | | | |

THUS far, we have confined the method to the analysis of impure materials, those containing two or more cations each above 1% concentration. (To fall in this category, organic and water samples are considered as their ashes.) An equally important problem is the analysis of a "pure" material, perhaps quartz, alumina, germanium, iron. The solution here involves the base material Spex Mix rather than the standards. The sample is first diluted with Spex Mix in several ratios and the spectra of each is compared with that of the original.

An example will clarify the procedure. Assume the analysis of a relatively pure sample of cerium oxide is required for other rare earth elements which may be present. We first dilute 0.956g of the cerium oxide (subsequently called "A") with 0.100g of Rare Earth Spex Mix to obtain "B". By doing this we added 0.500% of the 16 elements to the original sample. In other words, if there was 0.1% Er in the original, the "doctored" sample will contain 0.6%. If, on the other hand, the original was free of Y, B will contain 0.5% Y. Next we prepare C by diluting B with A in the ratio 1B:9A to add 0.050% of the rare earth elements. D and E are similarly prepared by successive dilution.

TABLE 3

*Analysis of Hypothetical Sample of Cerium Oxide
Using Rare Earth Spex Mix*

| Desig. Composition | Relative Intensity (0 not detected, 7 very strong) | | | |
|----------------------|---|-------------|-------------|-------------|
| | Dy 4046A | Er 3372A | Eu 4594A | Gd 3422A |
| A Original Sample | 6 | 0 | 7 | 0 |
| B 0.5% RE's added | 4 | 7 | 6 | 4 |
| C 0.05% RE's added | 2 | 4 | 6 | 2 |
| D 0.005% RE's added | 2 | 2 | 6 | 1 |
| E 0.0005% RE's added | 2 | 1 | 6 | 0 |

From the analysis cited in Table 3, Dy would be reported at 0.0x%. We notice that the intensity grades from A to B to C but that C, D and E have about the same intensity. The addition

NOBLE METAL G STANDARDS

| | | | |
|----|--------|-----|----|
| Au | 2428.0 | <5 | <5 |
| Ga | 2943.6 | 5 | 5 |
| Hf | 3194.2 | 50 | 10 |
| In | 3256.1 | 10 | <5 |
| Ir | 3220.8 | 50 | 10 |
| Pd | 3242.7 | 10 | 5 |
| Pt | 3064.7 | <5 | <5 |
| Re | 3460.5 | 50 | 10 |
| Rh | 3434.9 | 10 | <5 |
| Ru | 3436.7 | 100 | 10 |

of 0.05% at C resulted in an intensity change but the addition of 0.005% at D did not. In other words, there must have been at least 0.05% Dy in the original sample. Er in the original sample was not detected. But what is the limit of detection in the cerium oxide matrix? We note that Er is detected in E at 0.0005% added. We can thus report Er not detected, less than 0.0005%. The Eu picture shows that the sample is not too pure. The Eu 4594A line appears identical at the B, C, D, and E dilutions. Therefore, the original sample must have had at least 0.5% Eu. Like Er, Gd is not detected in the original sample. Unlike Er, however, it is not detected in E. It is reported: Gd not detected, less than 0.005%.

For the determination of common elements or Noble Metal elements, a like procedure is followed, mixing the unknown respectively with either Spex Mix or Noble Metal Spex Mix. Table 4 gives the proportions to be mixed for each of the three groups of elements. For simplicity, most spectrographers prefer to work with unit decimals and, accordingly, use the figures in the last column of the table.

TABLE 4

Analysis of Pure Materials

| Base | % of each element in base | Dilution to add 0.500% of each element | Dilution to add 0.100% of each element |
|----------|---------------------------|--|--|
| Spex Mix | 1.28 | 1 base + 1.56x | 1 base + 11.8x |
| RESM | 5.28 | 1 base + 9.56x | 1 base + 51.8x |
| NMSM | 9.32 | 1 base + 17.6x | 1 base + 92.2x |

Table 4 lists the concentration of each element added to the unknown (x) by the respective standard. Thus to add 0.100% of each of the 49 elements present in Spex Mix to an unknown sample, 11.8 parts of the unknown are added to 1.00 part of Spex Mix. If it is then desired to dilute down to 0.0100% of each added element, 1.00 part of the resulting material is mixed with 9.00 parts of the original sample.

WHEN first announced, precision figure of $\pm 30\%$ were reported for our Semi-Quantitative standards. Since that time, many spectrographers have indicated precision values as good as $\pm 10\%$, once procedures reserved for quantitative work were adopted. Although it is heartening to learn that, by spending more time on the problem, excellent accuracy can be attained, the spectrographer must always maintain a balance between the cost of the analysis, on the one hand, and its value on the other.

The method offering least accuracy gain but most speed makes use of master plates prepared under identical conditions as samples will be run. Here a minimum of preparatory work (see Bickford, H. J., Rowe, W. A. and Yates, K. P., *Anal. Chem.*, 34:1772, 1962) is rewarded by a rapid routine method since the standards need not be run on each plate. The main sources of error are the every-day variations in photographic processing, the emulsion itself, the temperature and humidity in the laboratory.

Advancing step-wise in accuracy, the following are some suggestions:

- 1) Weigh samples or pack electrodes more reproducibly with a machine such as the Spex Electrode Loader.
- 2) Take densitometric readings, convert to intensity and plot. Variations in burning may be compensated for by making measurements of the background in the vicinity of the lines.
- 3) Add an internal standard or measure intensity ratios to a suitable matrix line.

- 4) Prepare intermediate standards bracketing the concentrations in the unknown by diluting the existing standards. A suitable dilution factor is the square or cube root of ten.
- 5) Use the Enclosed Stallwood Jet in arcing samples.

Increasingly, the spectrographer is called upon to furnish a complete elemental analysis of a sample with as high an accuracy as he can achieve commensurate with the time savings expected over non-instrumental methods. In order to find out for ourselves and other users how best to go about handling such samples, we ran five standards by a technique modified for the purpose. (Table 5.)

The problem is many-faceted. A sample may run the gamut both in the number and concentration of anions and cations. Volatile, low ionization point elements may exist as impurities in a refractory base and vice versa. The need may be for a picture of the major elements and/or those at trace levels.

All considered, we decided to use the following:

1) Spex L Standards (No. 1004) mixed 1:1 with National SP-2x; -100 mesh graphite powder. Internal standardization was, of course, necessary and the Li_2CO_3 -based L Standards met this criterion. For refractory materials the addition of graphite prevented the formation of non-conducting oxide beads. The particular graphite chosen was easy to handle and weigh out and particles did not tend to fly out of the cup during arcing.

2) DC arc excitation with the Enclosed Stallwood Jet (Spex No. 9027, water-cooled). This combination has been shown by numerous spectrographers to result in a reduction in background in many areas of the spectrum. At the same time, by stabilizing the excitation, the Stallwood Jet thus offers real improvement in precision and accuracy. Eight amperes were used in the source and a flow rate of 9 cfh of a 30:70 mixture of oxygen:argon through the Stallwood Jet.

3) National SPK preformed electrodes. We have not seen data to substantiate this but are convinced that the superior physical uniformity of this grade of graphite should result in improved reproducibility. The sample electrode was an undercut 3/16" preform L-3706 (Spex No. 4004); the upper a pointed 1/8" preform L-4236 (Spex No. 4019).

4) SA No. 2 plate (the work was performed before the SA No. 3 emulsion was announced). Our reasoning here was to have a long, relatively shallow-sloped characteristic curve, uniform for all wavelengths. In the final figures, we limited our data to lines with transmittances in the range 10-70% because, as a simplifying compromise, we used but one internal standard line, Li 2741.2A. A three-step filter (Spex No. 1090) assured obtaining at least one step of each line in the specified transmittance bracket.

5) Dilutions of samples with the Li_2CO_3 graphite mixture of 1:9, 1:99 and 1:999. The rule followed was to choose the greatest dilution which would give spectral lines of the elements sought in the 10-70% transmittance range.

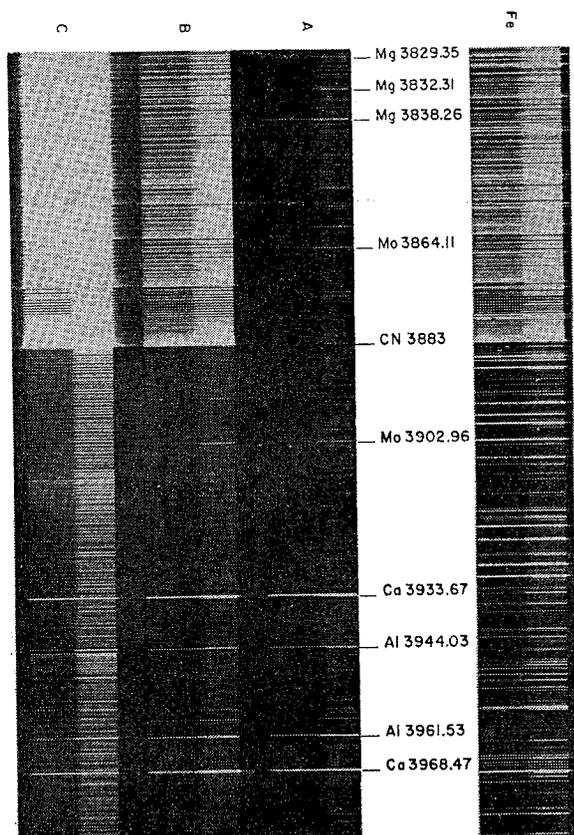
We have not treated the data statistically but, quite obviously, it would be regarded, on the whole as good, semi-quantitative information. If quantitative accuracy is required, probably the fluxing technique of Tingle and Matocha (see Vol. VI, No. 4 of the *Spex Speaker*) offers the best choice. The time and effort, however, well exceed that of the present method. Furthermore, since spark excitation is normally used on the pellets, obtained by pressing the flux together with graphite, sensitivity suffers.

TABLE 5

| ELEMENT | USGS G-1 | | USGS W-1 | | BAS MANGANESE ORE | | NBS LEAD BARIUM GLASS | | NBS BOROSILICATE GLASS | |
|---------|----------|-------|----------|-------|-------------------|-------|-----------------------|-------|------------------------|-------|
| | A | B | A | B | A | B | A | B | A | B |
| SI | 33.9 | 31 | 24.6 | 28 | 3.87 | 2.7 | 30.5 | 23 | 37.7 | 33 |
| CA | .97 | .87 | 7.8 | ----- | .557 | ----- | .15 | .16 | ----- | ----- |
| MG | .24 | .25 | 3.98 | 3.8 | .422 | .4 | .018 | .017 | .0157 | .012 |
| FE | 1.37 | 1.4 | 7.76 | 8.5 | 1.49 | 1.8 | .034 | ----- | .0532 | .05 |
| MN | .021 | <.05 | .14 | .18 | 51.3 | ----- | .068 | .064 | ----- | ----- |
| AL | 7.54 | 6.7 | 7.94 | 8.7 | .641 | .73 | .095 | .076 | 1.03 | 1.0 |
| TI | .144 | .16 | 1.647 | .85 | .012 | .03 | .06 | .10 | .016 | .01 |
| CR | ----- | ----- | ----- | ----- | .893 | .84 | ----- | ----- | ----- | ----- |

In Column A appear the % concentrations as standardized
 In Column B appear the % concentrations as determined

The first two standards are ground rocks prepared by the U. S. Geological Survey; the others are by the British Bureau of Analysed Samples, Ltd. and the National Bureau of Standards.



A, B and C are three spectrograms of the Spex G2 standards taken under almost identical conditions. The burning for C was made in an ordinary dc arc; in B an open Stallwood Jet was used with a 70:30 A-O₂ mixture; A was with an Enclosed Stallwood Jet (Spex 9027). Note the enhancement of many lines and freedom from background. Sensitivity is thus appreciably increased. Note, too, the reduction in the CN band in B and its complete elimination in A.

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DO YOU HAVE OUR PURE MATERIALS
 CATALOG? IF NOT, WE SHALL BE
 HAPPY TO SEND ONE ON REQUEST.

★ ★ ★

ROCK STANDARDS ANNOUNCED BY CAAS

The Nonmetallic Standards Committee of the Canadian Association for Applied Spectroscopy has standardized two samples which are now available for distribution. These are a sulfide ore and a syenite rock. Priced at \$5.00 per 1/4-pound bottle, each standard may be obtained from G. R. Webber, Department of Geological Sciences, McGill University, Montreal, Quebec. Remittances should be made payable in advance to The Canadian Association for Applied Spectroscopy, Non-metallic Standards Committee, and will be used not only to reimburse the CAAS for the development of the present standards but to foster further work of this nature. A report on the standards will be found in *Applied Spectroscopy*, 15, 159, 1961.

ADDENDUM

Inadvertently omitted from the last issue of the SPEX SPEAKER was reference to the pioneering work of J. E. Hawley and Graham MacDonald of the Miller Research Laboratory, Queen's University, Kingston, Ontario (*Geochimica et Cosmochimica Acta*, 10, 197, 1956) on the use of the Stallwood Jet for the analysis of rocks and iron ores. Shortly after publication of Stallwood's original article, these investigators corroborated the advantages of the device which is so well known today. Anticipating later studies, this involved the U. S. Geological Survey's G-1 and W-1 reference standards, with which the authors showed that determinations could be made within an experimental error of 5% using air in the Jet.

CURRENT STANDARDS PRICE LIST

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| <p>1000 Spex Mix. 49 elements, 1.28% each element. Ag Al As B Ba Be Bi Br Ca Cd Ce Cl Co Cr Cs Cu F Fe Ga Ge Hg I In K Li Mg Mn Mo Na Nb Ni P Pb Rb Sb Se Si Sn Sr Ta Te Th Ti Tl U V W Zn Zr2g \$ 36.00</p> <p>1001 Z Standards. 0.1%, 0.01%, 0.001% of 49 above elements in zinc oxide base (for analysis of organic materials).set \$ 33.00</p> <p>1002 G Standards. 0.1%, 0.01%, 0.001%, 0.0001% of 49 above elements in graphite base (for analysis of inorganic substances).set \$ 44.00</p> <p>4061 Graphite Powder, highest purity, -100 mesh. For use with G Standards.1 oz. \$ 6.00</p> <p>1003 Zinc Oxide, spectrographic grade.1/4 lb. \$ 8.00</p> <p>1004 L Standards. 0.1%, 0.01%, 0.001% of 49 elements in lithium carbonate base (for analysis of organic materials, particularly petroleum products).set \$ 36.00</p> <p>1234 Lithium Carbonate, spectrographic grade....10g \$ 6.00</p> <p>1006 Si Standards. 0.1%, 0.01%, 0.001% of 49 elements in SiO₂ base (for analysis of minerals).set \$ 33.00</p> <p>1250 SiO₂, 5-9s pure.10g \$ 4.00</p> <p>1007 Al Standards. 0.1%, 0.01%, 0.001% of 49 elements in Al₂O₃ base (for analysis of minerals).set \$ 33.00</p> <p>1212-4 Al₂O₃, 4-9s pure.20g \$ 3.50</p> <p>1008 Ge Standards. 0.1%, 0.01%, 0.001% of 49 elements in GeO₂ base (for analysis of high purity germanium).set \$ 36.00</p> <p>1227 GeO₂, 5-9s pure.5g \$ 8.00</p> <p>1009 Ga Standards. 0.1%, 0.01%, 0.001% of 49 elements in Ga₂O₃ base (for analysis of high purity gallium).set \$ 42.00</p> <p>1226 Ga₂O₃, 5-9s pure.1g \$ 7.60</p> <p>1012 In Standards. 0.1%, 0.01%, 0.001% of 49 elements in In₂O₃ base (for analysis of high purity indium).2g \$ 33.00</p> <p>1230 In₂O₃, 5-9s pure.10g \$ 5.20</p> | <p>1013 Ni Standards. 0.1%, 0.01%, 0.001% of 49 elements in NiO base (for analysis of nickel and its oxides in electronic tubes).set \$ 33.00</p> <p>1239 NiO, 3-9s+ pure.10g \$ 10.00</p> <p>1014 Ca Standards. 0.1%, 0.01%, 0.001% of 49 elements in CaCO₃ base (for analysis of minerals, particularly water deposits).set \$ 36.00</p> <p>1220 CaCO₃, 3-9s pure.10g \$ 5.00</p> <p>1020 Qual Mix. Proprietary mixture for qualitative spectrochemical analysis, 43 elements in a readily arced base, so blended that about three lines of each element will appear on the spectrographic plate in the region 2100 to 4700A.2g \$ 20.00</p> <p>1025 Qual Mix Atlas. Comprises 20 charts with spectra of Qual Mix, Fe arc and spark, taken with Hartmann diaphragm.each \$ 24.75</p> <p>1031 Rare Earth Spex Mix. 16 rare earth elements (includes scandium and yttrium) 5.28% each element: Ce Dy Er Eu Gd Ho La Lu Nd Pr Sc Sm Tb Tm Y Yb2g \$ 36.00</p> <p>1032 Rare Earth L Standards. 0.50%, 0.05%, 0.005% and 0.0005% each of 16 rare earth elements in Li₂CO₃ base.set \$ 49.00</p> <p>1033 Rare Earth Qual Mix. Preparation for qualitative analysis of 16 rare earth elements.2g \$ 20.00</p> <p>1041 Noble Metal Spex Mix. 10 elements, 9.32% of each: Au Ga Hf In Ir Pd Pt Re Rh Ru.2g \$ 38.00</p> <p>1042 Noble Metal G Standards. 0.50%, 0.05%, 0.005% and 0.0005% of each of 10 noble elements in graphite base.set \$ 48.00</p> <p>1010 Element Kit, individual compounds of 49 elements present in Spex Mix.kit \$ 48.00</p> <p>1030 Rare Earth Element Kit, individual compounds of 16 elements present in Rare Earth Spex Mix.kit \$ 50.00</p> <p>1040 Noble Metal Element Kit, individual compounds of 10 elements present in Noble Metal Spex Mix.kit \$ 50.00</p> |
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LITHIUM FLUORIDE vs. LITHIUM CARBONATE AS A BUFFER

by P. W. J. M. BOUMANS
University of Amsterdam, Netherlands

Many modern spectrochemical techniques involve dilution of the sample with a buffer, one of the most common being lithium carbonate/graphite mixtures. In our laboratory, we have recently undertaken a fairly detailed, systematic study (1, 2) of excitation conditions (temperature, electron pressure and background intensity) in dc graphite arcs containing varying metal vapors. Experimental and theoretical arguments indeed confirm that a lithium salt combined with graphite powder is most appropriate as an admixture in spectrochemical analysis (3). In the course of these investigations, a marked difference has been observed between the behavior of lithium carbonate, on the one hand, and lithium chloride or fluoride, on the other. Buffered with the carbonate, the arc tends to wander continuously on the outer walls of the filled lower electrode (anode), whereas chloride or fluoride dilution of the sample results in a smoother burning in most instances.

In order to arrive at a plausible explanation of these differences in behavior, it must be recognized that alkali halides are known to volatilize as the compound. By contrast, lithium carbonate decomposes in the electrode cavity to its oxide and CO₂. In graphite, the oxide is probably then reduced to the

metal which, in turn, might promote the diffusion of lithium atoms through the electrode walls. In view of the low ionization potential of lithium, its presence at the electrode surface may very well account for arc wandering.

Using lithium chloride or fluoride, a stable discharge can be obtained, especially in combination with the "stabilizing graphite ring" surrounding the cathode (1, 2, 3)*. Lithium chloride, being hygroscopic, the fluoride appears to be more promising, particularly since its high (1676°C) boiling point promotes steady volatilization. Especially is this true if fluoride/graphite mixtures, using excess graphite, are employed.

Obtaining lithium fluoride in sufficiently high purity had been one problem in our initial work. Later, the use of material supplied by Spex Industries proved entirely satisfactory. Detailed investigations of the physical properties of lithium fluoride/graphite arcs and their suitability for spectrochemical analysis are in progress in our laboratory. A number of interesting results will be published shortly.

1) Boumans, P. W. J. M., PhD thesis, University of Amsterdam, 1961.

2) Boumans, P. W. J. M., Colloq. Spec. int., IX, Lyon, 1961.

3) In preparation.

*Details of this technique will be given in a subsequent issue of the *Spex Speaker*.

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| 1134 Lithium Fluoride, 5-9s pure.10g | \$ 20.25 |
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INFRARED SPECTRA SOUGHT

Following is a letter we received from the English Group Editor of the DMS system. Butterworths, the publisher, is anxious to cooperate with "donors" and encourage the contribution of spectra. Since their announcement of the new Peep-hole Index ("I") Cards there has, of course, been a new surge of interest in the DMS infrared data card system. Publication of about 10,500 literature and spectral cards has now been completed and the first "I" Card issue covers 5,000 of these. The data cards are sold in volumes of approximately 2,000 each at \$196.00 per volume delivered in the U. S. The new "I" Cards are priced at \$65.00 per issue and deliveries are promised shortly for orders received at this time.

We, at Spex, shall be happy to answer any questions you might have regarding DMS as well as to accept spectra for contribution to the publication.

* * *

Dear Sirs,

Although hundreds of laboratories have subscribed to the DMS Index during the past six years, only a few have taken advantage of the opportunity offered by DMS to have their own spectra indexed. We are therefore writing to invite you to contribute spectra for publication in the DMS Index.

We are prepared, not only to index spectra for our subscribers, but also to supply additional personal copies of such cards for laboratory use free of charge and to meet any desire for secrecy to the extent of treating any contribution as anonymous, if that is desired.

Besides wishing to extend our range in organic spectra of all types, we are anxious to build up a useful nucleus of inorganic spectra and are particularly interested in the spectra of inorganic complexes and compounds of silicon, boron and phosphorus.

Selection of spectra for publication by the English editorial office of the DMS Index is in the hands of an honorary advisory scientific committee consisting of four of the leading spectroscopists in the U. K. This committee has laid down no general rules for acceptance except that spectra should normally be those of compounds of definite structure and that, as far as possible, the 3μ region of the spectrum should be covered as well as the more usual 5-15 μ region.

When we accept spectra from spectroscopists, our aim is to give as little trouble as possible to those who supply them. We accordingly accept spectral traces that are linear whether in wavelength or wave-number. Those that are linear in wavelength are converted by a distortion-camera to wave-numbers. Band tables are useful, but are not essential. If band tables are not supplied, we measure the eight strongest bands from the trace and give the wave-number on the card. If the purity of the sample has been established by element analysis an appropriate entry is made on the card. In other cases in which the status of a sample is that of a "research sample," it is desirable for the spectroscopist to give some physical property such as melting point. UV data are of interest to users of DMS cards and will be given on the card, if available.

Spectral traces require no re-drawing by their authors. Traces lent to DMS are copied and returned by registered mail. DMS has an arrangement with Kodak in London for micro-filming and copying spectra which facilitates their reproduction on cards. This takes about three weeks. If, however, the return of spectra is required urgently, they can be photocopied in our own machine and returned immediately by registered mail.

At present DMS is publishing only infra-red spectra of organic and inorganic compounds. Among inorganic compounds spectra of complexes are particularly desired. It is hoped to include Raman spectra later.

DMS is able to offer its contributors publicity comparable with that of the scientific journals. We accordingly like to give the name of the scientist responsible for the work, when spectra from academic and industrial collections are contributed. If authors so desire, reference to published papers can be given on our cards, whether the spectrum was actually included in the published paper or not.

The English editorial office of DMS will be glad to supply any further information to those wishing to contribute spectra to DMS.

I shall be grateful if you will kindly bring this to the notice of spectroscopists.

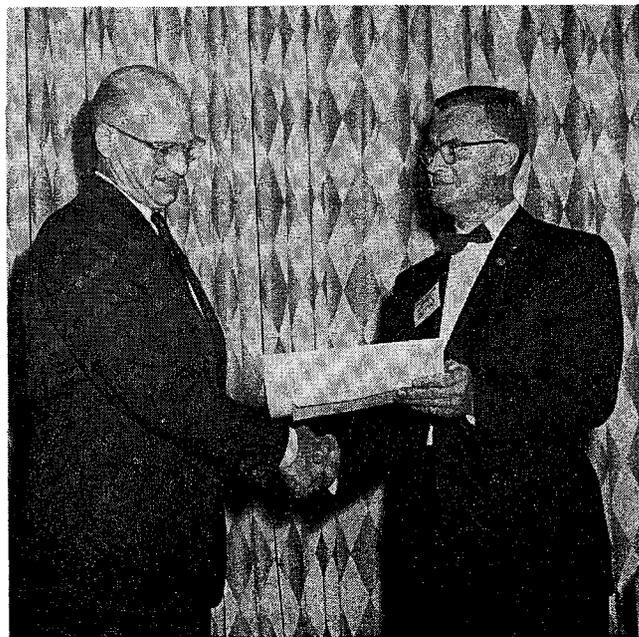
Yours faithfully,

DR. I. SANDEMAN

Managing Editor, English Group

DOCUMENTATION OF MOLECULAR SPECTROSCOPY

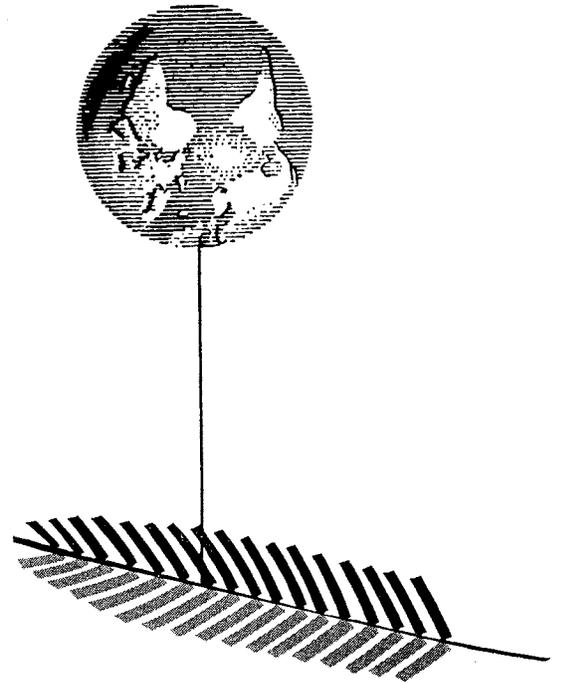
TED LEE ACCEPTS AWARD



For the comprehensive series of papers on "The Spectrographic Determination of U235" Mr. Lee and co-authors A. L. Hallowel, O. P. Killeen, S. A. MacIntyre, L. H. Rogers and S. Katz are recipients of the second annual Spex Industries sponsored SAS Journal Award. We are happy to note that the judges are finding it difficult to eliminate contenders for this award which was established to encourage and offer recognition of papers describing outstanding research or development work reported in *Applied Spectroscopy* during the preceding year. The 1962 winners, all with Union Carbide Nuclear Corp., Oak Ridge, Tenn., are to be commended particularly for their accomplishments in overcoming the many faceted problems connected with U235.

The presentation was made during the EAS in New York City, November 15, 1962, by John Hansen, President of SAS.

Season's Greetings



P. O. BOX 98 • SCOTCH PLAINS, N. J.

FOR YOUR INSPIRATION
FOR YOUR ENCOURAGEMENT
FOR YOUR COMPLIMENTS
FOR YOUR CONTRIBUTIONS OF DATA AND IDEAS
FOR YOUR PATRONAGE

We are about to move again and this too is Thanks to You! You have consistently kept us hopping in our efforts to maintain stock for immediate delivery of our standards, instruments and supplies. But don't stop now—we still need the exercise!

Our new facilities are planned to enable us to keep a step ahead of your requirements. Laboratory and engineering areas, particularly, have been enlarged as a result of the popularity of our "GISMO" (Grazing Incidence Spectrometer Monochromator) and its siblings.

Obviously, and understandably we hope, it is with pride that we are bursting out of our present confines. We hope you will soon write, call and/or visit us at our new home.

OUR NEW ADDRESS: SPEX INDUSTRIES, INC., 3880 PARK AVE., METUCHEN, N. J.

February 1, 1963

Phone: 201—549-7144



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