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SEMI-QUANTITATIVE SPECTROCHEMICAL ANALYSIS*

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Introduction

Direct or primary methods of measurement are generally easy to develop and not subject to error. Indirect or secondary methods are, on the other hand, notoriously unpredictable. To put it another way, measuring a length simply by measuring a length leads to an answer with which few people will argue. But measuring wind speed with a wet finger—or even a modern anemometer—often leads to disagreement.

The direct approach is usually involved in wet chemical analysis. We weigh x plus y and, at the last step, we weigh x alone. We then calculate that the concentration of x is $x/(x+y)$. As opposed to this, instrumental methods—including optical spectroscopy—are secondary. We can measure the intensity of a spectral line alright. But try to convince a wet chemist that this intensity means that a certain sample contains 1.2% silicon especially when his own result is 1.4063%!

To get around this problem of making indirect measurements, the usual procedure is to run comparison standards along with the unknown. The spectrographer begs or borrows analyzed samples and uses these as a frame of reference. For example, he brackets an unknown sample of 24S aluminum between two knowns and, using a sheet of graph paper and a straight edge, calls off his answers. But suppose the sample is not 24S aluminum; instead a material falling in the catch-all category of "gook." Then what? His standards no longer work. At 1.2%, the intensity of a particular silicon line is far different in a 24S matrix from what it is in the sample of gook.

The first thing a scientist does when he stumbles on a new problem such as this is to give it a name. This one was pompously christened "matrix effect." It is, in my opinion, the most significant—certainly the most economically important—problem in spectrochemical analysis. When a spectrographer finds a 24S sample on his desk, he polishes up the 24S standards and the unknown. In no time, he polishes off the analytical results as well. But let's return to that sample of gook, or perhaps sludge, precipitate, dust, corrosion deposit, ore, rock, slag or ash. What kind of standards can be used for these *complete* unknowns?

The Spex semi-quantitative standards are of course, the ones we recommend for such samples. To overcome the matrix effect, the technique used with these standards is one of dilution. For example, suppose the G (graphite base) standards are to be employed. The sample is first diluted with graphite in the ratio of, say, 1 to 9. The matrix is thus essentially converted to graphite—identical for unknown and standards alike. Seeing 90% graphite and only 10% sample, the spectrograph is fooled into giving reliable answers. The matrix effect is, in effect, bypassed.

But, before going into further details on these standards, it would be well to trace the history and development of semi-quantitative analysis. Fry (1) neatly classified the attempts at developing a universal method of semi-quantitative analysis under five headings:

1. Disregard the matrix effects.
2. Compare the unknown spectra with spectra of synthetic samples.
3. Correct for matrix effects.
4. Select internal standard for each element group.
5. Dilute unknowns with a large amount of some material, a) an alkali metal salt; b) other miscellaneous metal or metal salt.

As would be expected, the first of these is subject to the most error. Ignoring the matrix effect leads to little better than a *qualitative* analysis. Equally significant, an element reported absent may be present in sizable concentrations if the behavior of the matrix is ignored. Methods in category 1) are thus primarily of historical interest.

In 1938, Slavin (2) developed the so-called total energy concept. He postulated that, if a sample is burned to completion, the intensity of a particular line will be proportional to the number of atoms emitting it—in other words, the concentration. Burning nine different NBS samples to completion, he was able to obtain a straight-line plot of the density of the calcium 3179A line *vs.* the weight of calcium in the respective sample. On this basis, he tentatively conclude that *any* element in *any* matrix could be measured merely by determining the proportionality constant relating the line density to the mass of the element *under the conditions used in a particular laboratory.* Although Slavin did not succeed in developing a universal semi-quantitative method on this basis, he made an extraordinary contribution by showing how essential a complete burn is.

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The total energy concept having pointed the way to better semi-quantitative methods, others were developed, some along the lines of the second category as given above. For instance, suppose one has to analyze samples of Mesabi ore for trace elements. One carefully prepares a series of synthetic Mesabi ores varying the trace-element concentrations. Using these as standards, accuracy can be almost quantitative. The main drawback of this second approach is that such standards are almost useless for the analysis of, say, a KNP fertilizer for *its* trace-element content.

To summarize our appraisal of Methods 1) and 2), the former should be used for *qualitative* analysis only. The second, while extremely useful in specific applications, obviously begs the question. It presupposes that the general composition of the sample is known. Very rarely is this true.

When the importance of the matrix became apparent, workers sought means for circumventing its influence. Correcting for matrix behavior, the third approach, was that developed by Harvey (3). He made exhaustive studies of the effects on spectral intensity of a wide variety of common substances. These were then converted into correction factors and published in tables. The criticism of this system, like that of the previous one, is that it is not applicable to a *complete* unknown. One must have a good idea of the material being analyzed before knowing which correction factor to use. Moreover, Harvey's factors vary considerably depending on the characteristics of the individual spectrgraph.

We must, however, be fair by evaluating Harvey's technique historically and crediting him with a job well done. The method was developed specifically for the ARL spectrographs during World War II when these instruments constituted a large majority in the United States. The dispersion, mounting and the graing itself were as identical as mass production could make them. In these circumstances, the Harvey method served quite well. Later, when other spectrographs found their places in laboratories, that method lost ground. Attempting to extend is applicability, Harvey published correction figures for a large Littrow spectrograph. Today, because of the wide assortment of spectrographs employed and also the fact that the method is not applicable to *complete* unknowns, Harvey's technique is no longer extensively used.

The fourth approach is probably the most unwieldy as a general method. If one wants to determine calcium in an unknown, he first adds a known amount of an element resembling calcium, for example, magnesium. From the way in which the magnesium lines behave, he can correct for and therefore estimate the concentration of calcium. Again, although there are occasions where the method is useful, it has two shortcomings. It requires the use of a large number of internal standards for each sample; it precludes the determination of those elements which are themselves added as internal standards. But, like the Harvey method, it is frequently a handy method, especially when no standards are available and a proximate determination of a particular element is needed.

The last in our outline of techniques is the category into which the Spex method falls, i.e., dilution. Dating back to 1907, at least twenty papers in the literature make use of this technique. It is by far the most universally applicable, the simplest and least subject to error.

The basis of the Spex adaptation is a powder called Spex Mix. This consists of compounds (mostly oxides) of 43 common elements weighed out so that each element is present at exactly the same concentration. That is, 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 to yield 1.00g of calcium, etc. Separately, each compound is first ground down to —200 mesh and, after being weighed, the compounds are ball-milled for many hours to assure uniformity (4). The total weight of the 43 compounds divided by 43 gives a figure of 1.34% concentration for every element present.

The actual elements present in Spex Mix are listed below:

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

The G standards are made by diluting Spex Mix with high-purity graphite. The actual graphite chosen is United Carbon Products Co., UCP-2, —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. Standard G-1 contains 0.100% of each of the 43 elements. It is made by mixing 0.124 weight units of Spex Mix with 1.00 weight units of graphite. Containing 0.010% of these elements, G-2 is made by diluting G-1 by a factor of 10 with graphite. The procedure is repeated for G-3 and G-4, the last containing 1 ppm of the elements.

An unknown powder is brought into the laboratory. Let us proceed to analyze it hypothetically. 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%. The Hour-Glass mixer, or more conveniently, the Wig-L-Bug is recommended for the dilution operations. With the latter, a plastic ball shakes the materials to be mixed in a plastic vial electrically for 10-60 seconds. The shortest mixing time possible is desirable in order to keep the grinding action to a minimum.

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

- x the original unknown
- .x the original unknown diluted with graphite 1:9
- .0x the original unknown diluted with graphite 1:99
- .00x 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 the undercut UCP 105-S, a shallow crater electrode without undercut (4196), or a narrow (1/8″) diameter electrode (5440) 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 .00x since it was known beforehand that all elements were present below 10% concentration.

TABLE I

Hypothetical Example of Analysis Using G Standards

*Intensity of Spectral Lines**

Material	*Si* 2881*A*	*Cu* 3247*A*	*Ag* 3281*A*	*B* 2498*A*
x	7	2	0	0
.x	6	1	1	0
.0x	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

*Visual estimates of intensity: 0 is not detected
7 is very strong

Interpretation of this table would be as follows: the silicon at the 100 times dilution (.0x) 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 calculated 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 simply be 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 state that the boron content of the original sample, if present, is less than .001%.

Dr. E. S. Hodge, of Mellon Institute, has devised a scheme for reducing the number of exposures required. His laboratory serves a wide variety of ever-changing research projects and almost every unknown is unique. Rather than running a complete set of standards on each film, Hodge (5) uses a precalibrated density scale mounted inside the screen of the microphotometer as pictured in Figure I. Employing a matching technique, he assigns a figure from 0 to 7 depending on which step is best matched by the spectrum line in the sample. For example, suppose at the 1:100 dilution, the silicon 2881A line in a particular sample matches step 3. He refers to a conversion chart previously prepared and finds that 3 represents approximately the same concentration as the silicon content in G-2 or 0.01%. Multiplying by the dilution factor of 100, he reports approximately 1% silicon in the original sample.

Part of the conversion chart which we supply is shown in Table II-A. The most common spectral lines are chosen for each element but room is left for compilation of other lines. A typical data sheet used with this technique is shown in Table II-B. At the microphotometer, density numbers are assigned by visually matching the unknown line with a step on the Hodge Scale. Next, by referring to the conversion chart and remembering to multiply by the dilution factor, the approximate % concentration is inserted.

TABLE II-A

Conversion Chart (% Concentration from Density Number) for use with Hodge Semi-Quantitative Scale

Element	*W.L.,A*	*Density Number vs. % Concentration* 1	2	3	4	5	6	7
Ag	3281							
Al	3093							
As	2350							
B	2497							
B	5535							
Be	2349							
Bi	3068							
Ca	4227							
Cd	2288							
Ce	4187							
Co	3453							
Cr	4254							
Cs	4555							
Cu	3247							

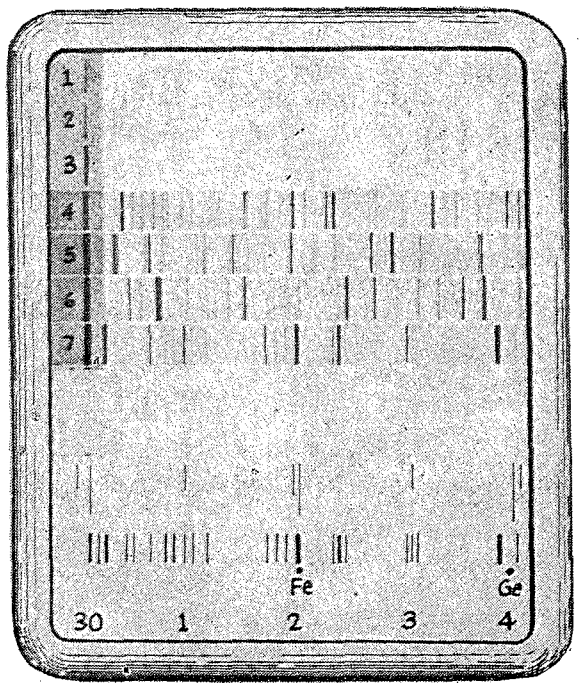

Figure I — Hodge Scale

Analysis of "Pure" Materials

Thus far, we have considered the analysis of impure materials consisting of a number of elements rather than essentially one. Another problem is the analysis of a pure material. Here the task is not only to determine the concentration of impurities present but also assign "less than" figures for those elements not found.

This solution makes use of Spex Mix itself. It is diluted with the sample in several ratios. A comparison of the spectra of the original material with the diluted materials is the basis of the method. An example will clarify this.

Let us call the sample to be analyzed "A". We first dilute 1.24g of the sample with 0.10g of Spex Mix. This, which we shall call "B", now contains 0.10% of all of the 43 elements added to the sample. (In other words, if there was 0.5% iron in sample A to begin with, B will contain 0.6%. If, on the other hand, the sample contained no germanium, then B will contain 0.1%). Next we dilute B with the original sample in the ratio

TABLE II-B

Data Sheet for use with No. 1100 Hodge Semi-Quantitative Scale

Sample Identification .....

Date..... Plate No. .....

Elt.	*W.L.,A*	*Den. No.*	*% Conc.*
Ag	3281		
Al	3093		
As	2350		
B	2497		
Ba	5535		
Be	2349		
Bi	3068		
Ca	4227		
Cd	2288		
Ce	4187		
Co	3453		
Cr	4254		
Cs	4555		
Cu	3247		

1B:9A. This we call C which adds 0.010% of the 43 elements to the original sample A. Likewise D and finally E are prepared by subsequent dilutions.

Table III gives the results to be expected in a typical sample:

TABLE III

Analysis of Hypothetical Sample of "Pure Material" Using Spex Mix

Desig.	*Comp.*	*Si* 2881*A*	*Cu* 3247*A*	*B* 2497*A*	*Zn* 3345*A*
A	Original sample	6	0	7	0
B	0.10% added	4	7	6	4
C	0.010% added	2	4	6	2
D	0.001% added	2	2	6	1
E	0.0001% added	2	1	6	0

*Visual estimates of intensity: 0 is not detected
7 is very strong.

In the above example, Silicon would be reported .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 of 0.01% at C permitted an intensity change but the addition of 0.001% at D did not. In other words, there must have been at least 0.01% silicon in the original sample.

Copper in the original sample was not detected. But what is the limit of detection in this matrix? We note that copper is detected in the lowest dilution, at 1 ppm and we therefore report: copper not detected, less than 0.0001%.

The boron content is interesting in that it shows that the "pure" material is really not pure, containing at least 0.1% of boron. The 0.1% addition and the 0.01% addition of boron appear identical on the microphotometer. Therefore, the original sample must have had at least 0.1%.

Like copper, zinc is not detected in the original sample. Unlike copper, however, it is not detected at the final dilution. It is reported: Zinc, not detected, less than 0.001%.

Organic Materials

Thus far we have described the analysis of miscellaneous and pure materials. Organic compounds fall in a third category mainly because of the necessity of ashing them before analysis. Either wet ashing or dry ashing may be employed; there are advantages and disadvantages to both. 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 will 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 shaken in the Wig-L-Bug or otherwise 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 in much the same manner in the standards as in 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 will 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 simply multiplied by the appropriate factor.

Although zinc oxide burns smoothly and reproducibly in a dc arc without the formation of a refractory bead, many people prefer to mix it with an equal quantity of graphite before burning. Such a procedure is that developed by G. W. Standen of the New Jersey Zinc Company. His electrode is roughly equivalent to UCP 5440 (a ⅛" diameter rod with a hole drilled to a depth of about ¼") and burnings are again made to completion. Sensitivity as reported by Standen is given in Table IV.

TABLE IV

SENSITIVITY OF ELEMENTS IN ZINC OXIDE*

Element	Wavelength A	Approx. % Detectable
Al	3092.7	.012
	3082.1	.02
	2575.1	.2
	2660.4	.3
Sb	2598.1	.04
	2877.9	.25
As	2780.2	.45
	2860.4	.6
Be	3130.4	.0006
	2650.5	.004
Bi	3067.7	.015
	2897.9	.15
B	2497.7	.002
	2496.8	.0025
Cd	3261.1	.55
Ca	3179.3	.02
	3006.9	.5
Cr	3021.6	.035
	2835.6	.04
	2849.8	.075
	2780.7	.4
Co	2407.2	.035
	2521.4	.035
	2648.6	.3
Nb	3094.1	.065
	2698.9	.2
	2740.2	.55
Cu	3247.5	.001
	3273.9	.0012
	2824.4	.35
Ga	2943.6	.03
	2719.6	.5
Ge	2651.2	.005
	2740.4	.75
Au	2675.9	.006
	2748.2	.2
In	3039.4	.045
	2710.3	.65
Ir	2664.8	.055
	2924.8	.065
	2849.7	.065
	2897.1	.65
Fe	3020.6	.01
	2723.6	.2
	2727.5	.6
La	3245.1	.35
	3265.7	.5
	2808.4	.95
Pb	2833.1	.05
	2614.2	.06
	2663.2	.5
	2823.2	1.1
Mg	2852.1	.0004
	2779.8	.055
	2782.9	.25
Mn	2794.8	.004
	2798.2	.012
	2949.2	.04
	2933.1	.075
Hg	2536.5	.03
Mo	3132.6	.03
	2672.8	.35
Ni	3050.8	.03
	2981.6	.085
	2984.1	.55
Pd	3242.7	.035
	2763.1	.3
P	2553.3	.3
Pt	3064.7	.015
	2705.9	.055
	2650.9	.15
Rh	3396.9	.2
	2703.7	.5
	2862.9	95
Si	2506.9	.004
	2631.3	7
	2987.6	4
Ag	3280.7	.0002
	3382.9	007
Ta	2714.7	15
	2661.3	35
Te	2385.8	.045
	2530.7	.45
Tl	2767.9	.03
	2916.3	.7
Th	2837.3	12
	2732.8	6
Sn	2839.9	025
	2863.3	045
	2661.2	6
Ti	3234.5	015
	3088.0	.04
	2956.1	35
	2641.1	.65
W	2724.3	04
	2944.4	045
V	3093.1	02
	2706.2	1
	2702.2	25
Zr	2678.6	.04
	2639.1	.4
Internal Standard:		
Zn	2712.5	
	2684.2	
	2670.5	

Accuracy

When the original work on the Spex standards was done, we published a precision figure of ± 30%. Since that time, many spectrographers have told us that they have attained ± 10% by taking densitometric readings and observing precautions ordinarily reserved for quantitative work, such as correcting for background, running samples and standards in replicate on the same plate, etc.

While it is good to know that, by spending more time on the problem, excellent accuracy may be attained, a balance between the *cost* and the *value* of the analysis should always be maintained. With this in mind, the following will show what returns can be expected from the least effort, the most effort and several in-between degrees of effort.

Undoubtedly, the simplest method of semi-quantitative analysis when any volume is involved is that devised by Hodge. A few hours spent in precalibration of the standards against a stepped intensity scale is rewarded by a large saving in time when samples are run. Hodge reports that, for 200 determinations on NBS samples, 90% of all concentrations found fell within the range 1/3 to 3 times the standardized values. Typical results are reported in Table V (5).

The scale itself (Cat. No. 1100) is shown in Fig. 1.

TABLE V

Analytical Results Using Hodge Scale

COMPARISON OF CHEMICAL AND SPECTROGRAPHIC ANALYSES

(Concentrations expressed as per cent of element)

U. S. Geological Survey Standard Samples

	G-1 (Granite)		W-1 (Diabase)	
	Chem.	Spec.	Chem.	Spec.
Na	2.4	1	1.5	1
K	4.5	1*	0.53	**
Si	33.7	>10	24.4	>10
Ti	0.15	0.1	0.67	1
Al	7.9	10	8.3	10
Fe	1.42	1	7.9	3
Mn	0.021	0.003*	0.13	0.01*
Mg	0.24	0.1	4.0	>3
Ca	1	1	7.9	3
B	—	—	0.0005	0.003*
Ba	0.13	0.1	0.027	0.03
Be	0.0002	0.0003	—	—
Co	—	—	0.0036	0.01
Mo	0.0008	0.001	—	—
Ni	0.0005	0.0001*	0.009	0.01
Pb	0.027	<0.01	—	—
V	0.0018	0.003	0.024	0.01
Zr	0.02	0.03	0.009	0.01

*Spectrographic value falls outside the ⅓ to 3X range of chemical value.

**CN band interference.

A variation of Hodge's method is to prepare a master plate (instead of an intensity scale) containing an entire set of semi-quantitative standards and run under conditions identical with those to be employed for uknowns. Lines on this plate are marked off to facilitate identification. While requiring a good deal of preparatory work, this method has an advantage in accuracy over Hodge's systems. The zinc line at 3345A, for example, will be just as diffuse on both the comparison and the unknown plates and the respective backgrounds will be equivalent, too. Matching is more exact than with the Hodge scale since one does not have to make mental corrections for differences in backgrund and/or line shape. Precision possible with this matching technique is perhaps such that the results will fall between ½ and twice the correct value.

The main sources of error in the second method are the every day variations in photographic processing, the emulsion itself, the temperature and especially humidity in the laboratory. All of these may, of course, be minimized by running the standards and unknows on the same plate. Transmittances may then be compared visually and results will be accurate within ± 50% of the amount present.

The techniques involved in squeezing out the optimum precision involve taking densitometric readings and plotting working curves. In this category, the simplest method is to plot % transmittance *vs.* % concentration on log-log paper. Alternatively, line-to-background ratios may be plotted with a significant gain in accuracy. In the Z and L standards, appropriate zinc or lithium lines may be used for internal standardization.

TABLE VI

Comparison of Wet Chemical and Spectrochemical Analyses Using Spex Standards

N.B.S. No. 88 (Dolomite)

Element	*Spex*	*Wet Chemical*
Silicon	0.12%	0.15
Aluminum	0.06	0.04
Iron	0.1	0.06
Magnesium	10	13
Calcium	15	21
Manganese	0.01	0.005
Titanium	0.006	0.003

Comparison of Wet Chemical and Spectrochemical Analyses Using Spex Standards

Welding Flux No. 12405

Element	*Spex*	*Wet Chemical*
Silicon	5.9%	6.5%
Iron	.60	.32
Aluminum	10.5	7.5
Manganese	15.0	13.6
Calcium	10.5	12.0
Zinc	3.5	3.6
Sodium	14.5	13.0

Comparison of Wet Chemical and Spectrochemical Analyses Using Spex Standards

Welding Flux No. 12407

Element	*Spex*	*Wet Chemical*
Silicon	10.0%	8.9%
Aluminum	5.6	3.6
Calcium	11.5	17.0
Chromium	6.0	6.3

Table VI gives typical results of analyses using techniques in the "middle" accuracy range. Here, transmittances are plotted as a function of concentration but no internal standardization is employed.

Table VII shows the kind of results to be expected when the best techniques are used to obtain the most accurate values. In this work, the following conditions were employed:

Spectrograph	3.4 meter Ebert, 15,000 lpi grating, 10-micron slit; step sector.
Source	dc arc, 6 amps; complete burn 3 min.
Plates	Eastman SA No. 1
Electrodes	105-S, 105-U (United Carbon Products)
Sample preparation	Wig-L-Bug, plastic vials
Standards	Spex L Standards ($LiCO_3$)
Calculations	Working curves using intensity ratios to Li 2474A; no background corrections required; four values averaged.

TABLE VII

Comparison of Wet Chemical with Spex Results on Bureau of Analysed Samples

Iron Ore No. 175

	Concentration, %		
	Spex	*Standard*	*Error, %*
SiO_2	6.2	8.13	13
Fe	55.8	58.2	4
MgO	1.73	1.22	41
CaO	2.32	2.05	31
TiO_2	.14	.12	16
Al_2O_3	1.86	1.83	2
Cu	.10	.037	162
Na_2O	.10	.10	0
K_2O	.20	.26	23
P	(less than) .1 n.d.	.056	
As	(less than) .05 n.d.	.011	

In addition, the Spex analysis estimated .0005-.005% of Mn, Pb, Cr, Ni, V, Zn, Ag, Co. These elements were not reported on the certificate accompanying the standard.

Conclusions

Procedures and standards have been developed for the semi-quantitative analysis of almost any material. Depending on the requirements, accuracy varying from semi-quantitative to almost quantitative may be achieved. Flexible and adaptable to a wide variety of spectrochemical problems, the methods are, nevertheless, straightforward and may be carried out on a routine basis by personnel with limited training.

Acknowledgment

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Literature Cited

1) Fry, D. L., *Bulletin,* A.S.T.M., 216:29, Sept. 1956.
2) Slavin, M., *Ind. Eng. Chem. Anal. Ed.,* 10:407 (1938).
3) Harvey, C. E., "A Method of Semi-Quantitative Spectrographic Analysis," App. Res. Labs., Glendale, Calif. (1947).
4) Mitteldorf, A. J., Landon D. O., *Applied Spectroscopy,* 10:12 (1956).
5) Hodge, E. S., Baer, W. K., *Applied Spectroscopy,* 10:150 (1956).

1000 **Spex Mix.** Base from which standards are prepared. This material is used for the analysis of "pure" chemicals. For this purpose it is mixed with the unknown to be analzed. It may also be used to prepare sets of standards of matrices other than those supplied. Each element in Spex Mix is present at 1.34% concentration.
per two grams **$36.00**

1001 **Z Standards.** 0.1%, 0.01% and 0.001% of above elements in zinc oxide base. Particularly useful for the analysis of organic materials.
per set of three, 2 grams each **$33.00**

1002 **G Standards.** 0.1%, 0.01%, 0.001% and 0.0001% of above elements in graphite base. General applicability, especially for inorganic materials.
per set of four, 2 grams each **$44.00**

4061 **Graphite Powder,** ultra purity, -100 mesh. For use with G Standards.
per oz. ..... **$ 8.00**

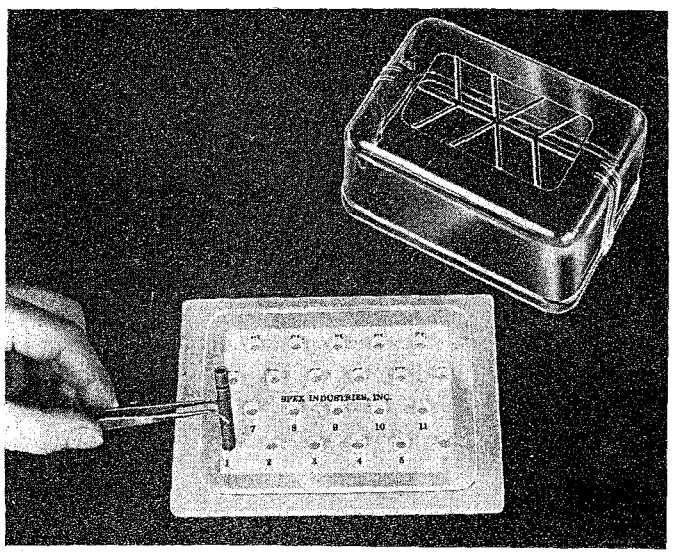
1003 **Zinc Oxide, spectrographic grade.** For use with the Z Standards as a diluent for unknowns.
per 15 grams ..... **$ 8.00**

1004 **L Standards.** 0.1%, 0.01% and 0.001% in lithium carbonate base. Used for the analysis of lubricating oils, crankcase sludges and other organic materials.
per set of three, 2 grams each **$36.00**

1005 **Lithium Carbonate, spectrographic grade.** For use with the L Standards as a diluent for unknowns.
per 10 grams ..... **$ 6.00**

1100 **Hodge Semi-Quantitative Scale.** Included with the scale are 100 data sheets, instructions and a set of conversion charts mounted in celluloid folders to protect them in use **$21.00**

1101 **Additional data sheets for above**
per 100 ..... **$ 2.80**



Plastic Electrode Stand

PLASTIC ELECTRODE STANDS

In response to your many requests, we are now manufacturing plastic electrode stands designed for loading up to 22 electrodes. Three stands are available for 1/4" d., 3/16" and 1/8" d. electrodes.

As pictured, the base of the stand is of Plexiglas and has 22 stations, each numbered to avoid mix-ups. The holes are so spaced that one of our funnels may be placed over an electrode without interference from an adjoining one. The base and clear plastic dust cover will resist mineral acids which might be accidentally spilled in filling an electrode.

In order to distinguish among two or three stands with which your technician is working, they are available in three colors: white, black and red.

Where the stand is to be used to dry electrodes, our Lazy Susan Electrode Stand is recommended. This instrument is machined of aluminum and anodized to protect it chemically. Each of its 24 stations may be rotated into position for ease in loading and individually covered with a transparent dust cover. By loosening a captive screw, the main table may be removed and placed in an oven to evaporate solutions from electrodes.

tricks of the trade

WIG-L-BUG TRICKS

Mr. E. B. Childs describes the use of the Wig-L-Bug by the U. S. Department of Public Roads, for breaking up soil aggregates prior to analysis. What is unique about his technique is his use of the steel ball (recommended for the steel vials) with the plastic vials. According to Childs, while the ball may break a plastic vial occasionally, the advantages are the very rapid preparation of soil samples directly in the container in which they are stored. Moreover, between-sample cleaning is entirely eliminated.

★ ★ ★

Sample preparation of zirconium and hafnium has been greatly improved using the Wig-L-Bug, reports F. Parks Landis of General Electric's Knolls Atomic Power Laboratory. Millings .003-.005″ thick are machined using a stream of inert gas, rather than a lubricant to cool the chips. These chips are placed in a silica crucible and ignited for several hours in a muffle furnace at 950°C. The resulting oxide flakes are so brittle that they are readily pulverized when shaken for 30 seconds in the standard plastic vials on the Wig-L-Bug. Mr. Landis claims that "spectrographic results for impurities in samples prepared this way are superior to those obtained from oxides derived from solutions. There is no possibility of loss of volatile compounds from solution and no contamination from mortar normally used to grind such samples."

★ ★ ★

Another unexpected use for the Wig-L-Bug has turned up. Kenneth T. Carolan of the Celanese Research Laboratories in Summit, New Jersey, has found that it offers much promise as a standard test for the high-frequency impact resistance of fibres. In this application, the fibres to be tested are placed in a stainless steel vial (3117) together with a ¼″ steel ball. Time necessary to break the fibres is used as an index of its impact resistance. Mr. Carolan reports that the figure-8 motion of the vial prevents the fibres from balling.

3051 **Plastic Electrode Stand, for 1/4″ electrodes,** white, black or red base (specify color)
Each **$20.00**

3052 **Plastic Electrode Stand, for 3/16″ electrodes,** white, black, or red base (specify color)
Each **$20.00**

3053 **Plastic Electrode Stand, for 1/8″ electrodes,** white, black or red base (specify color)
Each **$20.00**

3000 **Lazy-Susan Electrode Stand,** for 1/4″, 3/16″ or 1/8″ diameter electrodes (specify diameter)
Each **$62.00**

3001 **Funnel for filling 1/4″ electrodes**
3002 **Funnel for filling 3/16″ electrodes**
3003 **Funnel for filling 1/8″ electrodes**
Each **$2.50**
Per dozen (state how many of each diameter) **$24.00**

3020 **Hotplate,** for drying electrodes on **No. 3000.** Stainless steel case with cast aluminum surface plate; completely variable control with indicating pilot light; 600 watts, 115-volts, 25-60 cycles (Temco).
Each **$19.75**

NEW PHOTOGRAPHIC EMULSION ANNOUNCED

April 1, 1957

A new photographic emulsion has been reported[1]. Since it shows great promise for spectrographic purposes, we are detailing its characteristics here. The emulsion, Panutopian-X, has a range of 2000-10,000A at a speed equivalent to Eastman's 103-0 in the UV. Although its sensitivity is so phenomenally high, its graininess is superior to that of SA No. 1. Further, it is claimed that the emulsion is hard, not subject to scratching, may be dried rapidly without distortion and has low chemical fog.

Because of its unusually long spectral range, a series of filters is available for use with it. Suppose on a grating spectrograph it is desired to photograph the region 4000-5000A, cutting out interfering second order lines at 2000-2500A. To do this, a filter is used at the slit. It has about 90% transmittance from 2500- to 10,000A and a sharp cut-off below 2500A. Similarly, other band-reject filters are available for almost any 500A region.

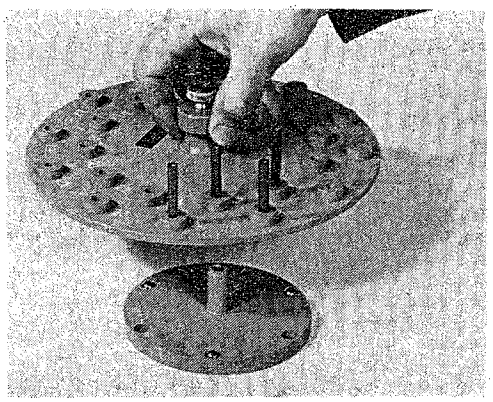
Another advantage claimed for the new emulsion is that the H&D curve is a straight line without the usually bothersome curved knee and shoulder. Taking advantage of this feature, the spectrographer merely plots transmittance values directly against percent concentration. A perfectly straight line working curve is thus obtained over as many as four logarithmic cycles. Plate calibration is eliminated and the calculating board may be disposed of as well.

But perhaps the most striking characteristic of the emulsion is that its gamma is set solely during development. That is, any gamma value between 1.0 and 3.0 may be obtained over the *entire spectral range* simply by using the proper indicator in the developer. If one desires a contrast of, say, 2.0, he adds a drop of the proper indicator to the developer. At the moment the indicator changes from green to bright gold, the proper contrast is reached and the plate is promptly "stopped."

[1]Westman, K., *Proc. Soc. of Imag.*, Vol. 1, p. 432 (1957).

* * *

No, we don't stock the above emulsion and probably won't. We *do* stock the common Eastman Kodak emulsions, however, such as SA No. 1, SA No. 2, 103-0, 103-F, I-L, I-N, 103-0UV, 103a-0. All plates and films are kept in deep freezers to maintain their shelf life and assure you of batch-to-batch uniformity.

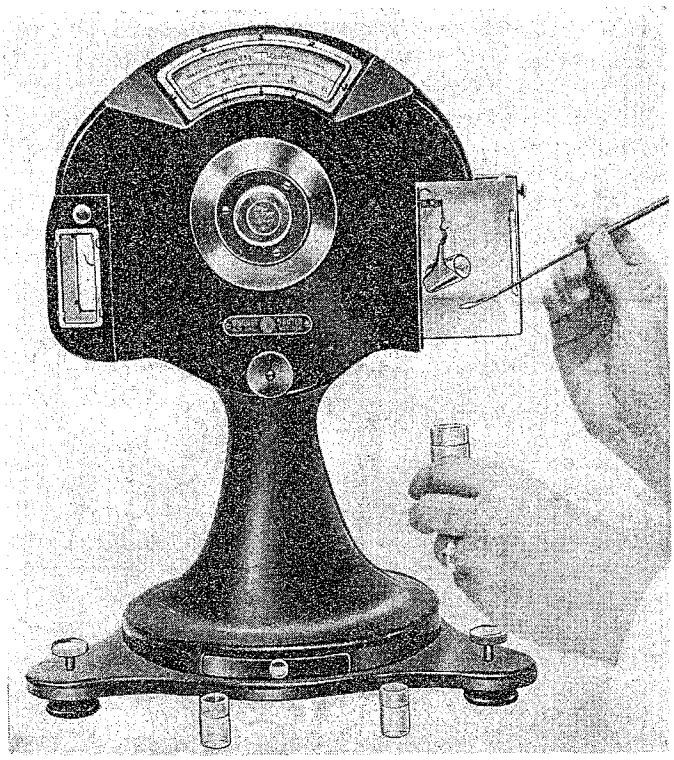


Lazy Susan
Electrode Stand

The ULTRA-MATIC PRECISION BALANCE

simple, rapid operation:

with a little practice an untrained person can make a single weighing in 5 seconds, or can weigh a powder directly into a plastic vial in 15 seconds.



SPECIALLY ADAPTED FOR USE WITH

The Crescent WIG-L-BUG
(Patented)

single knob control:

covers the entire weighing range.

no weights required:

from zero to capacity of reading scale.

no friction or bearing surfaces:

the patented suspension system eliminates pivots and bearing friction.

The Sauter Ultra-Matic Precision Balances are ideal for the spectrographer—emission, x-ray and infra-red. They are capable of weighing the small quantities of materials used in a matter of seconds, with all the accuracy he requires. In addition, the balances are fitted with a weighing pan designed specifically to hold the ½″ d. x 1″ long plastic vials used in the Wig-L-Bug electric mortar.

Just place the empty vial in position, tare it and then preset the balance for the desired weight of charge. Then add the material to the vial until the balance is in equilibrium. The entire weighing can be accomplished in fifteen seconds.

Although the Ultra-Matic Balance is available in various capacities ranging from 1 mg up to 12.5 grams, the optimum instrument for the spectrographer is either the 250 mg or the 500 mg model fitted with a range extension to permit weighing up to five times the reading capacity. This is necessary to permit taring of the vial, which weighs about 1100 mg. Thus the 500 mg model, with range extension, will weigh up to 2500 mg total capacity with the final 500 mg of weight directly readable without weights to 0.5 mg equal to one-half of one scale division. Again, with the spectrographer in mind, a 10 mg sample can be weighed to a precision of five percent of the amount being weighed.

To assess your own needs, first determine the *minimum* sample weight you encounter. If you weigh out as little as 5 mg, then you will require the 250 mg model to attain weighing precision of five percent. This model, with range extension, will permit you to weigh up to 1250 mg capacity. If your weighings are to be made in the plastic vial, the maximum sample weight would be about 150 mg.

If, on the other hand, your minimum loads are 10 mg, the 500 mg model will be more suitable. With this instrument, you can weigh a maximum of 2500 mg, or about 1400 mg directly into the plastic vial.

7000 **Sauter Ultra-Matic Precision Balance:** 250 mg model, with range extension permitting weighing up to 1250 mg capacity. Includes special weighing pan designed to hold ½″ dia. x 1″ long plastic vial (3111); a round pan; weight for checking linearity of reading scale; 2 x 250 mg and 1 x 500 mg weights for weight range extension and a pair of horn tipped tweezers; vinyl dust cover **$260.00**

7001 **Sauter Ultra-Matic Precision Balance:** 500 mg model, with range extension permitting weighing up to 2500 mg capacity. Includes special weighing pan designed to hold ½″ dia. x 1″ long plastic vial (3111); a round pan; weight for checking linearity of reading scale; 2 x 500 mg and 1 x 1 g. weights for weight range extension and a pair of horn tipped tweezers; vinyl dust cover **$260.00**

WE INVITE INQUIRIES ON THESE BALANCES IN CAPACITIES RANGING FROM 1 MG UP TO 12.5 GRAMS. ALSO AVAILABLE ARE SPECIAL ADAPTATIONS OF THIS MODEL WITH SEPARATE WEIGHING COMPARTMENTS WHICH MAY BE EASILY WASHED DOWN FOR USE WITH RADIOACTIVE MATERIALS.