

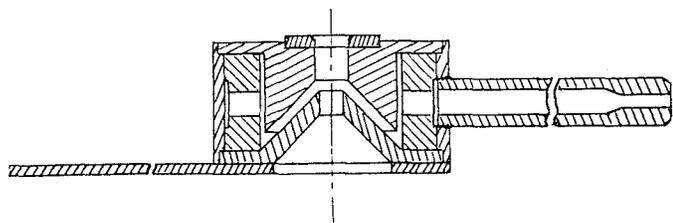
THE STALLWOOD JET: PROGRESS REPORT

WERE you one of us experimenters who, a few years back, spruced up the ornament on the front end of the family auto with a bug deflector "guaranteed" to woosh all of the insects clear of the windshield? Or did you, like this editor, think about installing a little traffic light in the rear window to signal green, yellow or red to the fellow behind and so keep him at a safe distance? Both of the problems were—and unfortunately still are—real. The solutions were wholly inadequate. Like so much other automobile gadgetry, they did not pass that all-important test of time.

The lesson carries over into the laboratory. Ingenious instrumentation is devised and proudly displayed each year. While much of it proves worthwhile, a sizable percentage either fails to solve the problems or introduces worse ones. Slowly but surely, such devices disappear from the market leaving the problems to linger tenaciously.

Take arc instability in spectrochemical analysis. The literature abounds in articles describing techniques to overcome it. Proposed, but largely unaccepted have been: magnetic devices to spin the arc at a constant rate; optical devices to produce multiple images of the arc column and so reduce the wandering by a factor equal to the number of images; cored electrodes; center-post electrodes; servomechanisms to keep the arc image centered on the slit. Despite the number and variety of so-called solutions, none seems to have gained a foothold in more than a few spectrochemical laboratories.

In 1954, however, a relatively obscure paper was published by a spectrographer named Stallwood who, at the time, worked at the Mines Branch in Ottawa. He proposed that the arc could be stabilized by sheathing it in an external curtain of air. Like so many other articles, it went almost unnoticed for several years until Stallwood's colleagues and others in Canada improved on the device and passed on their enthusiastic comments. Stallwood's jet became the famous Stallwood Jet so widely accepted and employed in hundreds of laboratories for as many diverse applications. We now have its history first-hand from Hal Champ whose later design was patented in Canada.



One of the earliest Stallwood Jet designs in which the assembly swings horizontally.

An Account of the Development of the Stallwood Jet*

W. H. CHAMP, *Geological Survey of Canada, Ottawa, Ont.*

BACK in 1949, which seems rather a long time ago now, Ben Stallwood and I were both working in the spectrographic laboratory of the Mines Branch at Ottawa, under the direction of Dr. M. H. Haycock. My concern at the time was mostly with metals and alloys, but Ben had the problem of establishing methods for "samples in general." The laboratory then, as now, received a weird and wonderful assortment of samples to be analyzed for most of the elements in the periodic table. A sign on our door proclaimed, "Satisfaction guaranteed or your sample back!"

In the course of his investigations into various methods for semi-quantitative spectrographic analysis, Ben came up with the idea of controlling a direct current arc by surrounding it vertically with a current of air. Using a small diameter electrode, this would cool the lower electrode (containing the sample) below the incandescent tip, would sweep away the cloud of vapor surrounding the arc itself and would stabilize the discharge column. A great deal of development work followed from this original idea.

The results of Ben's preliminary investigations were described by him at the Pittsburgh Conference in March 1951 (1). This was followed by the submission of his thesis to the University of Toronto in June 1951 (2). In 1951-52 the work continued with the assistance of two other laboratory members, Frank Lang and Robert Sturrock. The first published account, covering results obtained to June 1953 appeared in a paper by Stallwood in 1954 (3).

To evaluate the comparative merits of various general semi-quantitative methods, ASTM set up a group under the chairmanship of D. L. Fry. This group prepared five test samples in different matrices and sent them to a number of laboratories for analysis in 1953-54. The results were reported at the Pittsburgh Conference in 1955 and in a following ASTM bulletin (9). The analyses submitted by Frank Lang using an air-jet semi-quantitative method developed in the Mines Branch Laboratory were as good as, or better than, those of all other methods of similar coverage. Unfortunately, Lang left the Mines Branch in 1955 and Sturrock in 1956 and their further work (5, 7, 8) has not been published.

Stallwood's jet control was not originally intended for use with electrodes larger than one-eighth inch in diameter, nor with sources other than the dc arc, nor for cathode layer appli-

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cations, etc. As he has said (3), "A controlled source of excitation has been developed to eliminate selective volatilization and element interference effects encountered in the spectrochemical analysis of powders with the dc arc." It did not completely succeed but I have yet to find any better general approach for practical use in analysis of powdered materials. Doubtless many modifications have been made for other applications, but that is another story.

The final Mines Branch jet control apparatus, although small and compact, was of a rather complex design, being composed of a number of precisely machined parts necessary to guide and control the gas flow. After considerable experimentation, I was able in July 1954 to devise a very much simpler model which has since proven entirely equivalent in performance. This was described at the Ottawa Symposium in 1955 (6). However, at that point I became embroiled in administrative complications familiar to government employees, which prevented further publication. A patent was subsequently granted on this design in 1958 (11).

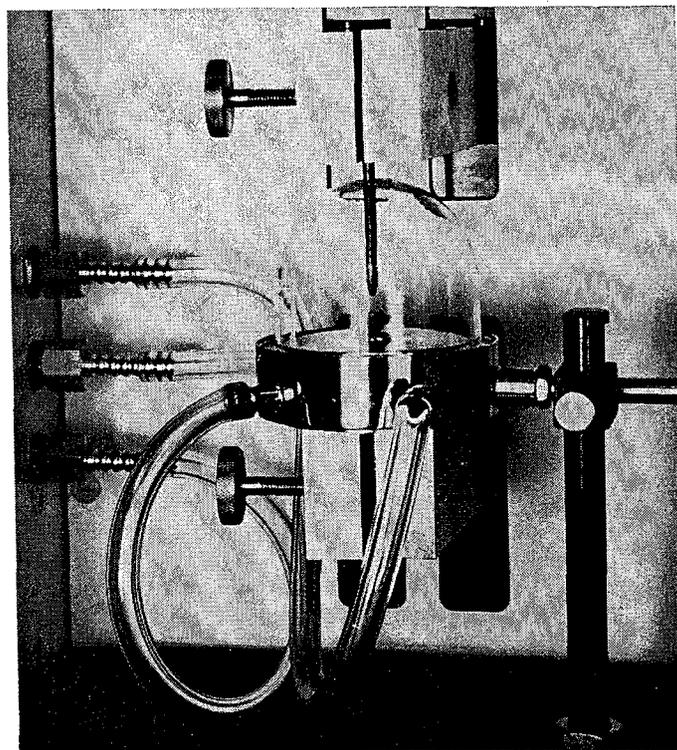
As the budding spectrographer soon finds out, everything affects everything else. With the jet accurate alignment of electrodes is required, since considerable lengths, both upper and lower, may be consumed. Also accurate centering of the drilled electrode crater and close control of diameters are necessary. Eccentric burning because of misalignment can cause quite erratic results. Fortunately, preformed electrodes and improved arc stands are now available so that these mechanical requirements can be met with comparative ease nowadays.

Having overcome mechanical and alignment problems, one can then use the jet-controlled arc in a wide variety of analytical applications. The proper combination of gas type and flow rate, current value, sample matrix, buffer, charge amount and proportions, exposure level, spectrograph or spectrometer, and so on (and on, and on . . .) can increase line-to-background ratio, reduce self-absorption, practically eliminate selective volatilization, except perhaps for some extreme refractories, and altogether produce excellent sensitivity and precision in the analysis of powdered materials. (Unfortunately, the inverse is also true! It is not too difficult to so adjust some of the variables involved that the resulting spectra are worse in all respects with a jet-control than without.)

As first described by Shaw (13), it is fairly easy to position a simple glass chamber on top of the jet control so as to nearly exclude air and using a N_2 -free atmosphere, practically eliminate cyanogen bands. Even without this addition an adequate reduction in cyanogen band emission can be obtained by using CO_2 , $A-O_2$ mixtures, etc., instead of air (18, 26). This probably depends a great deal on the amount of projection of the sample electrode tip above the orifice of the jet control.

Arc control devices very similar in general intent have been described by Ansell and Helz (31), Philcox (28), and Sinclair, Beale and Sharkey (29, 30). The construction, where details are given in these and other references (17, 21, 23) varies considerably. So far, to my knowledge at least, no one has correlated all the principles involved. However, studies of the basic factors affecting dc arc processes which these devices are intended to control are beginning to appear more frequently in the literature. As observed by Ahrens and Taylor in their book, page 65 (22), "There is much scope for investigations of fundamental properties (for example, temperature and degree of ionization) of the air-jet discharge."

These various controlled dc arcs can be considered at least first cousins to the recently developed "plasma jet," about which articles are rapidly being published. There is a large and growing literature on excitation in controlled atmospheres,



Spex Enclosed Stallwood Jet No. 9027

with enclosures around the arc being of most frequent mention. The bibliography following does not include these related subjects, of course. Also, articles in which Stallwood's work is given only brief comment have not been included. The unpublished items are given here mainly to show the continuity of development. Many people have obtained information about these techniques by personal contact with the authors.

ALTHOUGH the Jet needs no introduction to most of us, perhaps, in the interest of completeness, a brief description is in order. The picture above shows the Spex version. Gas is forced into a swirl chamber and then upward through an orifice surrounding the sample electrode. As the electrode burns away, it may be advanced with respect to the curtain of gas. Instead of having the gas enter the open atmosphere as it leaves the orifice, it enters a quartz enclosure where, by building up a slight positive pressure, it excludes the ambient gas, particularly nitrogen. Illumination from the arc is through a small window in the side of the enclosure.

The choice of gas is a subject of much current discussion but the need to eliminate N_2 and so cyanogen bands is universally accepted. Many spectrographers have settled on a 70:30 $A-O_2$ mixture. Cyrus Feldman of the Oak Ridge National Laboratories uses $He-O_2$ mixture to determine trace elements in ashed human tissue and Be in air dust and smears. R. L. O'Neil (32), AC Spark Plug Division, Flint, Michigan, chose CO_2 for a similar Be problem. O'Neil's analytical results are typical of the improvement in accuracy associated with the use of the Jet:

Comparison of Accuracy with and without Stallwood Jet

Sample	Be present micrograms	Be Determined, micrograms	
		With Jet	Without Jet
G-1	2.3	2.3	1.3
Al_2O_3	50	51.	55.
13% Al_2O_3	20	20.	40.

Studies on the Analysis of Tungsten Using the Stallwood Jet

E. C. SNOOKS, *Linde Company, Indianapolis 24, Ind.*

Although an inert gas may be used without supporting oxygen, resulting burning time is very long and, indeed, may never go to completion. Recognizing this, Edward Murt, Philco Corporation, Lansdale, Pa., analyzes cadmium fluoborate by first treating it with ammonia gases to produce a mixture of ammonium fluoborate salts and cadmium hydroxide. After drying, the sample is burned for 15 seconds in a dc arc employing an A sheath. The remainder of the sample is burned with air blown through the Jet.

One of the characteristics of the Jet claimed by Stallwood and since corroborated by many others is the decided reduction in matrix effect permitting much more reliable semi-quantitative procedures than heretofore. A single set of standards often suffices for all of the materials so analyzed. The last issue of the SPEX SPEAKER reported on such a semi-quantitative method as it applied to a variety of well established standards. It is not surprising therefore that others are using the Jet to handle their semi-quans. R. I. Quigley, Kawecki Chemical Company, Boyertown, Pa., finds that, for the analysis of high-purity magnesium fluoride, it affords "greater reproducibility and sensitivity" at the same time reducing "cyanogen band interference particularly for the determination of Sr." In his method a mixture of the sample and Li_2CO_3 in the ratio 3:1 is burned in a shallow crater electrode first at 10 amps and after 10 seconds at 20 amps. A 70:30 A-O₂ mixture is used at a rate of 5 lpm. Simple visual comparison with a master plate affords the required accuracy for production control, eight elements being determined in the range 20-100 ppm.

ENHANCED sensitivity reported so often with the Stallwood Jet appears to be of two kinds. One, naturally, is when the persistent lines of the elements are hidden in the cyanogen bands. The actual *raies ultimes* are, of course, dependent on the gas used and differ considerably when, say, straight A is used in place of conventional air. Nevertheless, the sensitivity of such elements as Mo, the rare earths, and Fe is enhanced often as much as ten times when a N₂-free gas is used. Murt reports that in a He atmosphere, the sensitivity of Ga in micro samples of In-Ga alloys is significantly improved.

The other reason for improved sensitivity relates to volatility. The excitation efficiency of a sample can be markedly increased if it is forced to burn slower. When a sample is placed in a deep-cratered electrode, the gas from the Stallwood Jet maintains the bottom of the sample cool, presenting the arc column with a slow stream of material. J. E. Van Dien, SpectroChem Laboratories in Franklin Lakes, N. J., points out a typical example of this. The sensitivity for As and Se—both highly volatile—in water ash is nicely enhanced, he reports.

While employed at the Vitro Chemical Company in Chattanooga, Tenn., O. I. Joensuu (now at the University of Miami, Coral Gables, Fla.) and N. H. Suhr (now at Pennsylvania State University, University Park, Pa.) devised a method for the analysis of rare earth and scandium oxides (15) first using CO₂ as the blower gas in a Stallwood Jet and later an 80:20 mixture of A-O₂ to increase the sensitivity of the rare earths determined. Pure rare earth and scandium oxides are mixed with graphite 1:2, then packed into a 1/8" diameter electrode with a crater 0.4" deep and burned in a 15-ampere dc arc at positive polarity. Excellent cross-correlation between these and analytical data by x-ray fluorescence is reported.

Joensuu and Suhr thus illustrate the practical significance of the Stallwood Jet in the quality control of a product manufactured by their company. Similarly, the following paper shows its advantages for keeping tabs on the trace-element level of Mo in W.

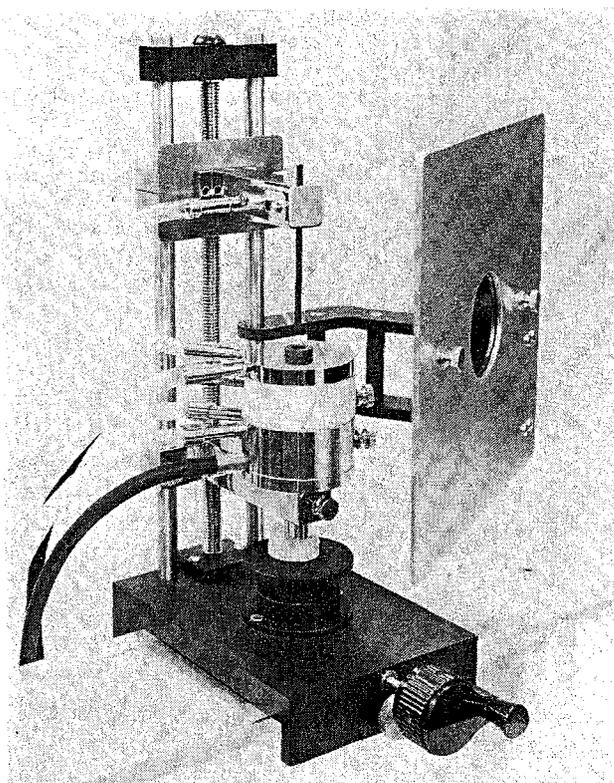
A VERY useful and highly promising use of the Stallwood Jet has been noted in the analysis of high purity W. This has always posed great problems for the spectroscopist because of its great abundance of spectral lines, the presence of a strong continuum and its refractory nature.

The last property has often been used to advantage though, in the elimination of many of the matrix lines.

Most investigators have been unable to use the strongest lines of Mo (3798.25 A, 3864.11 A) because of the presence of the cyanogen bands; hence a loss of sensitivity. In spite of the reduction of background brought about by the formation of WC, much is left to be desired. These two problems can be solved by employment of the Stallwood Jet and an inert atmosphere.

Investigations in this laboratory have shown that the use of an A-O₂ atmosphere and the Stallwood Jet will eliminate the cyanogen bands in this valuable region of the spectrum and further reduces the W continuum. The gas ratios studied and found most effective, cover the range of 80:20 to 60:40 A-O₂. Such mixtures, introduced through the jet at a flow rate of about 7-10 lpm allow an even burn, without unduly prolonging the burn time, and produce enhancement of many impurity lines.

Thus, a solution has been established to the problems inherent to spectral analysis of this system. The use of the jet in combination with the described gas mixtures provides an unusually stable dc arc for greater reproducibility of results. This system used in conjunction with a carrier technique should provide improved sensitivities with high precision.



Spex Plasma Jet No. 9030 (for use with solutions) mounted in custom-built stand for use without an Arc/Spark Stand.

WHEN A. J. Lincoln and J. Kohler of Engelhard Industries, Newark, N. J. set up their Stallwood Jet for the analysis of high purity Ag, they sought only the combination of stability and sensitivity reported by others. What they achieved (33) in addition was help in a clean-up problem always associated with arcing of silver nitrate. Spattering in all directions, it has a nasty habit of depositing tenaciously everywhere. Acid or cyanide solutions must be used to remove it. With the Enclosed Stallwood Jet, most of the silver deposits inside the quartz dome, from which it is readily removed. Ag samples in any form are first converted to silver nitrate then loaded into a medium deep crater electrode 3/16" dia. Arcing is at 12 amperes using pure A as the flushing gas. The authors report a sensitivity gain of at least one order of magnitude for Au, Ir, Pd, Pt and Rh (down to fractional ppm) when the quartz dome is used on the Stallwood Jet.

They have also extended the use of the Stallwood Jet to the analysis of high-purity Pt (34). The sponge is first ground to a powder in plastic vials using a Spex No. 5000 Mixer/Mill, after which it is mixed with graphite powder and pelletized. The procedure is especially noteworthy in its sensitivity for As down to 20 ppm and Zn down to 10 ppm, again illustrating enhancement of the Jet for volatile elements. Limits of detection of most of the other elements fall in the 1-10 ppm range while Ag, Rh and Au are detectable down to fractional ppm.

Seeking a correlation between sensitivity and the gas used J. T. Peters and M. Lalevic of the Drexel Institute of Technology in Philadelphia reported (35):

"There is considerable discrepancy in the literature in explanations for the effect of gaseous atmospheres on the intensity of spectral lines. Many factors, such as matrices used, temperature changes and volatilization time brought about by the use of gases, are believed by some researchers to be responsible for the enhancement of some spectral lines. The experimental data are inconsistent, however.

"It was our goal to try to find some criterion which would enable us to say that the enhancement of spectral lines will or will not take place under given circumstances. We studied spectral lines of ten different elements in four different gaseous atmospheres and compared the signal-to-noise ratios to those in air. Investigating the influence of different factors we found that one can say with certain confidence that the most influential single factor on the enhancement of spectral lines is the correlation between the excitation potential of the line analyzed to that of the gas used. By grouping spectral lines according to their excitation potentials, we observed that enhancement of spectral lines took place when the excitation potentials of the lines were near the excitation potentials of the gases used. In an A atmosphere, for example, the enhancement always occurred when the excitation potential of the line was near 13 ev, i.e., to that of A."

As examples, Peters and Lalevic measured the signal-to-noise ratios of two Mg lines one (Mg 2852A) having an excitation potential of 4.3 ev, the other 12.0 ev. Results for two different matrices follow:

Spectral Line	S/N in A	
	CaCO ₃	Al ₂ O ₃
Mg 2852A	0.52	0.73
Mg 2801A	4.2	12.7

PROBABLY more than any other single spectrographer, Prof. Denis Shaw has studied, improved and reported on the Jet. It must be remembered that, originally, Stallwood proposed air and for several years it was referred to as an air

jet. Determined to pile the advantage of improved sensitivity on that of precision and reduction in matrix effects, Shaw tried other gases and combinations. His work and that of his students are highly regarded.

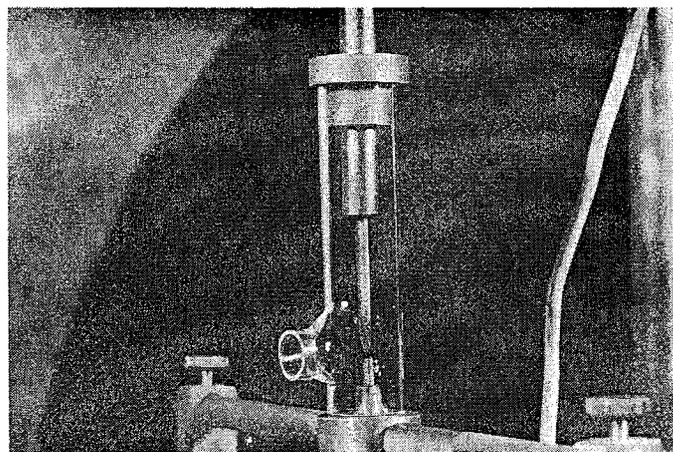
Spectrographic Methods Using the Stallwood Jet

D. M. SHAW, *McMaster University, Hamilton, Ont.*

AT McMaster University, Geology Department, analyses are all made by dc arc techniques and for the past eight years the Stallwood Jet has been used for almost every quantitative problem. Separated mineral or rock powders are customarily mixed in a 1:1 ratio with graphite containing Pd and In as internal standards, and burned in 1/8 inch graphite electrodes. Lithium carbonate and other buffers are occasionally used as well as or in the place of graphite.

The first impressions gained in using the Stallwood Jet were not very favorable. Using compressed air the cyanogen background was very intense and the gains in precision which resulted from a better controlled burn were offset by loss in sensitivity, by comparison with ordinary techniques. Completed studies (36, 37) however demonstrated the value of the device in permitting satisfactory precision (5 to 15% of amount present) to be obtained for simultaneous determination of a dozen elements at concentration levels from 10-1000 ppm.

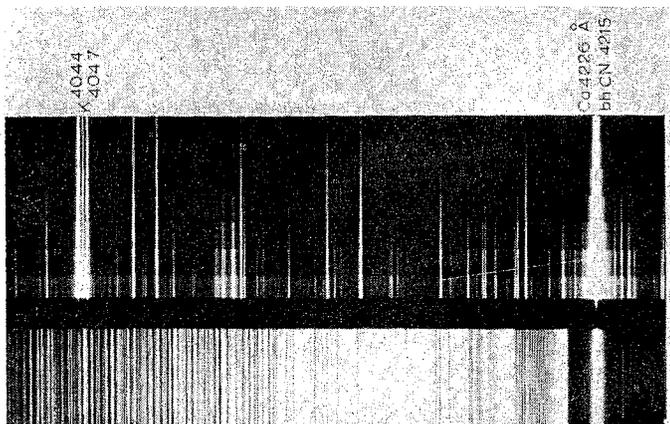
Later studies, still with air, extended the number of elements determined to 18, using several lines of more abundant elements to permit determinations to levels greater than 1%. At the same time B. J. Stallwood's original claims of drastic reduction of matrix effects were confirmed, at least to the extent that the same working-curves were found to be suitable for the analysis of scapolite (38), pyroxene (39), igneous rocks ranging from gabbro to granite (40) and greywacke (41).



Shaw's jet assembly and chamber (1958).

The continuing desire of the spectrographer to improve his methods led, however, to concurrent attempts to reduce cyanogen background. All manipulations of sample-buffer mixtures having failed, it was decided to attempt the obvious, namely to exclude nitrogen from the arc. This led to experiments with various controlled atmospheres, resulting in the adoption of a simple glass chamber to isolate the arc from the air, while supplying a mixed flow of A-O₂ (13). The results were very satisfactory, in that (a) background decreased spectacularly in the region 3400-4215A, (b) lines such as Ga 4172A, Pb 4057A became available for use, (c) the sensitivity of most elements increased.

A 1:1 gas mixture was used in the first studies. Subsequently, J. N. Weber (25) showed that pure oxygen gives satisfactory results with a very much shorter exposure time (2 seconds). Our recent experience has confirmed the satisfactory features of Weber's method although we now find complete combustion in oxygen to require 12 to 15 seconds. However, it appears that the sensitivity of many elements is markedly lower in pure O₂ than in A-O₂ mixtures (e.g. Ni 3414A could not be detected at a concentration of 100 ppm using pure O₂), and the A proportion is rather critical. After a series of tests by E. F. Cruft, W. Chesworth and A. M. Kudo in this laboratory we have settled on an A-O₂ ratio of 80:20. We now purchase the gases ready-mixed (Canadian Liquid Air Co. Ltd., Hamilton, Ont.), which gives much better reproducibility than with the previous system where two tanks were used. The substitution of the Spex Industries Arc/Spark Stand for home-made equipment has likewise helped to make the rather critical operational procedures easier to carry out.



Lower spectrum is of graphite in air. Upper spectrum is of a silicate, taken with the jet and an A-O₂ mixture, showing absence of CN band lines.

At present several trace-element studies are being carried out, and the individual methods are being modified and fused into another general method for silicates, using A-O₂ in place of air atmospheres. We have learned to mistrust the intensities commonly quoted for arc lines, since at the high arc temperatures obtained with use of the jet, it is usual to find ion lines much stronger than atom lines: for example, Sr 4077 Å is markedly more sensitive and reliable than Sr 4607 Å. In the carbon-rich mixtures which permit such high temperatures we also find strong enhancement of the sensitivity for Be and Ag, both of which can be measured down to at least 0.5 ppm.

The improved sensitivity obtained with the gas mixture chosen permits the use of gauze screens to reduce background to the point where, although corrections are still applied, it is possible to use self-calibration of each spectral line in each exposure, thereby improving precision. This would be time-consuming for graphical methods, but by restricting transmission readings to the range where the Seidel function will give a straight-line calibration curve (i.e. transmission values of between 5 and 80) it is feasible to use the university's Bendix G-15 computer. Programs have been written to accept transmission readings on 2 or 3 adjacent steps of the spectrum, calibrate the plate, make background corrections and type or punch out the log intensity ratio of analysis to internal standard line (y values). A separate program will calculate the working-curve (regression equation) for sets of spectra prepared from standards of known composition, and test the straight line obtained for deviations from linearity by regression analysis. If this is then modified by incorporating the constants of the work-

ing-curve it will provide punched card output in ppm of the analysis element. Samples are analyzed in triplicate and the analytical precision is computed (in logarithmic units) by pooling the variances for batches of up to 100 or more samples, thereby obtaining much more realistic estimates than those previously obtained by, say, analyzing a single sample 10 times.

The table which follows contains four replicate analyses of the well-known rock standard W-1 together with the mean values and the best estimate obtained by other authors (taken from Ahrens & Fleischer in *U.S.G.S. Bull.* 1113, 1960). Systematic errors are suspected for Sc and Ni but the other values are satisfactory.

Replicate Analyses of W-1

	(ppm)							
	Cr	V	Ni	Co	Sc	Sr	Ba	Zr
	102	245	49	37	26	160	152	93
	115	167	51	37	20	208	224	87
	110	264	58	40	23	202	185	105
	129	193	54	33	15	206	248	84
\bar{x}	114	217	53	37	21	194	202	92
R	120	240	82	38* 51*	43	175* 220*	225	100

* Alternatives

ONCE nitrogen in the atmosphere is eliminated, can it be determined? was the question J. T. McQuade of Carborundum Refractories Division Plant in Fords, N. J. asked. Preliminary results appear quite favorable. His company produces a super refractory called Refrax, a silicon-nitride bonded silicon carbide. The sample is first pulverized in a hardened tool steel mortar to pass through a 149 micron sieve. Placed in a 3/16" necked crater electrode it is arced at 10 amps in a Stallwood Jet using 3-5 lpm of an A-O₂ mixture. A preflush for 20 seconds is followed by a burn to completion in 70 seconds. With chemically analyzed samples, a reproducible working curve was plotted in the range 1.0-10% N₂. Although further experimental work is needed to ensure the confidence in the initial investigation, one wonders about the possibility of determining N₂ in organic materials. Proportional to the protein content, N₂ determinations are of great significance in the food industries. Mr. H. H. Selby of the American Agar and Chemical Company, San Diego, California uses the Jet on organic materials but, as far as we are aware, not, as yet, for the determination of N₂.

Selby's work is, nevertheless, quite significant. He states, "Whereas we once found it necessary to make three exposures per sample to obtain estimates of the quantities of 14 elements and 30 interferences present in agars and intermediates, we can (with the Jet) get information on 16 elements and 34 interferences with one exposure per sample. Apparently, specificity and precision are improved by factors of two and three, respectively." For a typical polysaccharide sample, 200 mg are mixed in 4 ml of lime water. After ashing, this is mixed with Li₂CO₃ and graphite to which small amounts of Ag, Pd and In are added as internal standards. Selby prefers to alternate A and O₂ in his procedure rather than use a mixture of the gases. He believes that, "improved consistency of our results may be due in part to the use of a relatively cool argon preburn, followed by the much hotter oxygen burn. Complete elimination of N bands is achieved, arc wandering is virtually eliminated and the sample burns to completion very smoothly."

INSPIRED by the potentialities of the Jet, E. S. Hodge and a group of other emission spectroscopists in the Pittsburgh area have decided to pool their talent and share their experiences and conclusions. The group has made their own jets of various designs. Hodge, of Mellon Institute, writes:

"In designing jets to achieve the Stallwood effect, several have been built which permit some of the gas to strike the electrode fully 1/2" below the jet orifice. This has a different effect from the Spex Jet in that a lamellar column of gas surrounds the electrode up to the arc. It was achieved in the Spex Jet by cutting off the conical section of the lower portion of the jet assembly and using a ceramic insert in the upper portion in place of the stainless ring supplied. Such an insert is non-conducting and makes it possible to bring the arc to within 2 mm of the jet orifice. Lavite, a machinable ceramic, has worked very satisfactorily for such an insert and is available from the S. M. Steward Mfg. Co., Chattanooga 1, Tenn. It has the advantage that the impinging gas strikes the electrode nearer the arc than the Spex design permits."

WE would like to express our grateful thanks to the representative group of spectrographers who contributed the information compiled here. We also invite comments, questions and rebuttals from our readers so that such may be published in a subsequent issue of THE SPEX SPEAKER.

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Preparation of Briquets for X-Ray Analysis By Lithium Borate Fluxing Technique

(Abstracted from paper delivered by MR. HARRY J. ROSE, JR., U. S. Geological Survey, Washington, D. C. at Conference on Spectroscopy, College Park, Md., June, 1962)

The procedure to be described is used for the quantitative analysis of silicate rocks by x-ray spectroscopy. The sample, fluxed in a graphite crucible, is ground, boric acid added and finally briquetted. It is compared with standards similarly prepared.

0.125g of sample, 0.125g La_2O_3 and 1.00g $\text{Li}_2\text{B}_4\text{O}_7$ are mixed in a boron carbide mortar for about 1 minute, then transferred to a graphite crucible and fused at 1000° for about 8 minutes. La_2O_3 serves as a heavy metal absorber (U. S. Geol. Survey Professional Paper 450-B, 1962 by H. J. Rose, Jr., I. Adler and F. J. Flanagan). If the sample contains large amounts of water or CO_2 , a preheat at 700° should be made. After cooling sufficient boric acid is added to the bead to bring the weight to 1.300g. This serves to cancel out any ignition losses between samples and also as an aid in binding the final briquet.

After being shattered, the bead plus the boric acid are placed in a tungsten carbide vial and ground for 10 minutes in a No. 8000 Mixer/Mill. Four such samples may be ground simultaneously using an adapter for the purpose.*

A small, unweighed amount of boric acid is hand pressed in a 1-1/4" dia. mold. This becomes the back of the final pellet serving to reinforce it and facilitate its removal and handling. The sample—boric acid mix is spread on top of the backing and a pressure not lower than 50,000 psi is applied. Lower pressures may result in a loss of intensity for the lightest elements. (On a 1-1/4" dia. pellet, the RH-30 press we supply has a capacity of about 49,000 psi. We also supply a somewhat smaller die, 1.235" dia. which may be pressed up to about 51,000 psi in the RH-30 press. The latter die is evacuable and is recommended for vacuum spectrometers where an unevacuated pellet has a tendency to explode.—Ed.)

Although not mentioned by Mr. Rose, a number of other spectrographers have found that, by spraying the final pellet with an acrylic lacquer such as Krylon, it may be kept moisture-free.

* Although Mr. Rose uses the No. 8000, the No. 5000 Mixer/Mill, a smaller instrument, may be used for the purpose, too. The latter can accommodate but two samples at once. Its grinding action may be somewhat more vigorous than that of the No. 8000, probably requiring a shorter grinding time.

SPEX INDUSTRIES PRODUCTS APPLICABLE TO THE FLUXING TECHNIQUE

3205	Boron Carbide mortar and pestle, 1-1/2" dia., 3/4" deep	\$268.00
8000	Mixer/Mill, 115 vac.	\$345.00
8000	Mixer/Mill, 230 vac.	\$353.00
8011	Adapter, for holding 4 No. 5004 vials in No. 8000	\$ 15.00
5004	Tungsten Carbide grinding vial	\$ 30.00
5000	Mixer/Mill, specify 115 vac. or 230 vac.	\$143.00
7150	Furnace, temp to 1100° , specify 115 or 230 vac.	\$145.00
7151	Rack and Handling Tongs for 7152 crucibles	\$ 19.00
7152	Crucible, graphite	100 \$ 20.00
	300	\$ 45.00

tricks of the trade

Grinding Asbestos in the No. 8000 Mixer/Mill

C. W. HUGGINS, *Norris Metallurgy Research Laboratory,
U. S. Bureau of Mines, Norris, Tenn.*

I have found the Spex Mixer/Mill very advantageous for grinding asbestos fibers for X-Ray Fluorescence Spectroscopy. We normally use our instrument for the determination of elements above atomic number 16. Many of the asbestos samples have 0.1-2.0% Ni, Cr, Fe, Ca and K and grinding in the Spex mill greatly facilitates the analysis. About the only other way to grind them is in a Wiley mill and this never reduces the size small enough for a good analysis in the X-Ray spectrograph.

No special recipe is used for grinding. We simply take a few chunks of selected fibers (free of all foreign contamination) and grind them about 10 minutes in the No. 8001 hardened tool steel vial. Iron pickup is less than 0.05% and this has little effect on the total iron content of the sample.

Some of the sample is also used for X-Ray diffraction to establish positive identification of the fibers. Our X-Ray man says that grinding in the Mixer/Mill also helps reduce somewhat the preferred orientation pattern that always results from X-Ray diffraction on fibrous samples.



Electron micrograph of chrysotile fibers showing open tubes before grinding.

My original idea, however, for reviewing chrysotile fibers after they had been ground in the Mixer/Mill was in hope of finding some short length fibers standing on end and to obtain a "doughnut" picture.

As is evident in the electron micrograph, I was not successful as the fibers are still too long for any to stand on end. My interest in doing this resulted from a paper by Pundsack a few years ago, in which he stated that single fibers could hardly be tubular for chrysotile because of the high density he measured. Pundsack's paper led many to believe that some artifact might exist and even though single fibers appeared tubular in the electron micrograph, this was not the case. Maser, about two years ago, did show the doughnut picture for a single fiber. He used a microtome to cut several cross sections. The accompanying photograph is surprising in that all of the tubes appeared flattened after grinding. This shows the great flexibility of chrysotile fibers. It also shows how efficient the bouncing ball in the Mixer/Mill really is as it certainly hit each fiber many times.



Electron micrograph of chrysotile flattened and broken fibers, after grinding in the Mixer/Mill. High magnification shows individual fibers actually 150-300A in diameter.

Plastic Grinding Vial

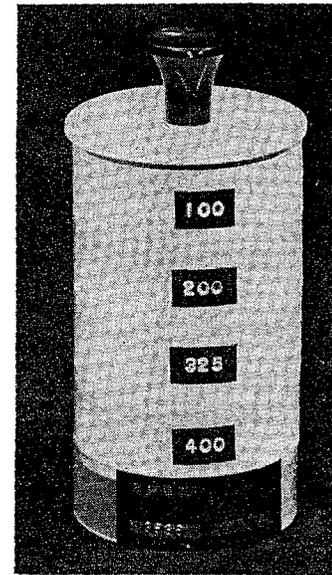
An all-Lucite grinding vial is now available for use in the No. 8000 Mixer/Mill. Capable of grinding such friable materials as antimony, bismuth, germanium, platinum sponge, beryllium oxide, silicon, and silica, it has already proved indispensable in the semiconductor field where such samples must be ground without a trace of metallic contamination.

8006 Lucite Grinding vial, with 1/2" dia. Lucite balls; grinding capacity about 20 ml. \$ 20.00

6005 Lithium Tetraborate, anhydrous	100g	\$ 4.00
	Lb.	\$ 11.50
RH30-1 Hydraulic Press		\$555.00
3622 Die, 1.250" dia., non-evacuable		\$215.00
3623 Die, 1.235" dia. evacuable		\$245.00
3624 Vacuum Pump, Welch Duo-Seal 1400B, 115 vac.		\$148.00

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Every step in the handling of high purity materials is a potential source of contamination. Our nylon sieves were designed to eliminate one such source of metallic impurities. Each sieve consists of a sheet of monofilament nylon cloth stretched in an "embroidery" frame consisting of two telescoping Lucite rings. The cloth, available in four mesh sizes, meets ASTM specification E11-58T for size and uniformity of mesh.



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| 3536 | Sieve Set, consisting of 4 frames and 1 tray with 1 each of the above screens | Set \$ 36.00 |
| 3530 | Sieve frame, consisting of two telescoping Lucite rings, 70 mm dia. x 25 mm high | Each \$ 9.00 |
| Screen, nylon monofilament cloth, 85 mm square: | | |
| 3531 | 100 mesh (each opening 149 microns) | twelve \$ 6.00 |
| 3532 | 200 mesh (each opening 74 microns) | twelve \$ 8.00 |
| 3533 | 325 mesh (each opening 44 microns) | six \$ 6.00 |
| 3534 | 400 mesh (each opening 37 microns) | three \$ 7.50 |
| 3535 | Tray, plastic, 70 mm dia. x 25 mm. high | Each \$ 4.00 |

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