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Maintenance. In the course of our studies, relatively little maintenance was required to keep the instrument in calibration. The long-path cell was periodically cleaned with ethanol each month during use to minimize ozone losses within the cell, a ten-minute operation. This procedure had no effect on the calibration and served to increase the light intensity reaching the detector and thus to reduce the integration period. Because an ultraviolet absorption technique is used, no accessory gases or solutions were required and the calibration was independent of small changes in the atmospheric gas flow rate. The ozone scrubber should be periodically changed as recommended by the manufacturer to eliminate the possibility for low ozone readings.

Airborne Operation. In airborne use, two important factors which must be overcome are aircraft vibration and tilt for noise-free and effective operation. With liquid-based measurement techniques, these factors tend to disrupt the flow of the measuring liquid and may cause noise excursions on the output recorder. Under the operating environment of a twin-engine aircraft (Cessna 401), this instrument has proved itself to be insensitive to these factors except during severe turbulence after which recovery was observed to occur in one 11-second measurement period. At a ground speed of 180 mph, the ozone measurements are integrated over a distance of 0.05 mile, with new readings every 0.5 mile.

Based on studies at ambient concentrations, there were no apparent interferences due to nitrogen dioxide, hydrocarbons, or sulfur dioxide. Possible interference would depend upon such factors as the value of the absorption and scattering cross sections at 2537 Å and the selectivity of the ozone scrubber. The sample intake was located in the aircraft nose approximately four feet in front of the propeller plane to eliminate exhaust-hydrocarbon interferences, and

no further interferences were observed in the course of our studies. The general agreement of the Model 1003 ozone measurements and the Mast total oxidants meter during each flight indicates that the levels of photochemically generated aerosols which were encountered did not introduce an observable change in the ozone reading. On one occasion an O₃-ethylene chemiluminescent monitor was flown with the Model 1003, and readings of both instruments were generally in agreement within 0.01 ppm of ozone at the low ozone concentrations that were encountered.

CONCLUSIONS

Based on the data presented in this report, the following conclusions can be made. The accuracy, repeatability and linearity of the ultraviolet absorption technique are satisfactory for atmospheric monitoring. The unit responded to within 98% of the step ozone input within one measurement period (11 seconds). The instrument proved itself to be sufficiently rugged and reliable for routine airborne operation. The use of the ultraviolet absorption technique results in a lower maintenance requirement as compared to liquid techniques for ozone measurement and either a comparable or lower maintenance requirement as compared to ethylene chemiluminescent techniques.

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CORRESPONDENCE

Beryllium Content of NBS Standard Reference Orchard Leaves

Sir: A recent paper (1) indicated the presence of volatile beryllium compounds in National Bureau of Standards Orchard Leaves (SRM 1571), and in air samples taken from a beryllium machining facility. Samples of Orchard Leaves digested with nitric and sulfuric acids in an open beaker, or dry-ashed in an oxygen plasma furnace at 150 °C, gave only 16% and 7%, respectively, of the beryllium content found when the leaves were digested under reflux with nitric and sulfuric acids (0.11 ± 0.01 ppm Be). Relatively large amounts of beryllium were detected in a Dry Ice cold trap inserted between the plasma furnace and the vacuum pump. The analytical method used involved gas chromatographic measurement of the beryllium trifluoroacetylacetone complex extracted into benzene.

This report (1) contained several surprising results. Among these was the observation that volatile beryllium compounds were present both in Orchard Leaves and in air samples taken from a beryllium machining factory. Also, the volatile beryllium compound detected in Orchard Leaves was so inert that it distilled from concentrated mineral acid mixtures, yet apparently underwent

complete chemical exchange with trifluoroacetylacetone (Htfa) when shaken for 15 min with a benzene solution of Htfa. This type of behavior is certainly unusual, and is not shown by any known beryllium compound (2, 3). For example, the beryllium complexes of acetylacetone and its fluorinated derivatives are very volatile and thermally stable, yet they are readily wet-ashed in an open beaker without any loss of beryllium (4-6).

Over the past ten years, a very large number of environmental samples have been analyzed for beryllium in our laboratory, after either wet-ashing in open beakers or dry-ashing at temperatures up to 800 °C (7). If undetected

(1) M. S. Black and R. E. Sievers, *Anal. Chem.*, **45**, 1773 (1973).

- (2) L. E. Smythe and T. M. Florence, "Recent Advances in the Analytical Chemistry of Beryllium," in "Progress in Nuclear Energy," C. E. Crouthamel, Ed., Series IX, Vol. 3, part 6, Pergamon Press, New York, N.Y., 1963.
- (3) D. A. Everest, "The Chemistry of Beryllium," Elsevier, Amsterdam, 1964.
- (4) J. D. Cosgrove, J. Morgan, and P. Pakalns, *Australian At. Energy Comm. Rept. AAEC/TM 87* (1961).
- (5) C. W. Sill and C. P. Willis, *Anal. Chem.*, **31**, 598 (1959).
- (6) J. K. Foreman, T. A. Gough, and E. A. Walker, *Analyst (London)*, **95**, 797 (1970).
- (7) W. R. Meehan and L. E. Smythe, *Environ. Sci. Technol.*, **1**, 839 (1967).

volatile beryllium compounds are indeed present in most environmental materials, our results would be invalid. Black and Sievers' paper also raises serious questions about health and safety aspects of the handling of beryllium and its compounds. We therefore set out to carefully check the beryllium content of NBS Orchard Leaves.

EXPERIMENTAL

Ashing Procedures. Samples of NBS Orchard Leaves (5 grams), taken directly from a freshly opened bottle, were ashed by the following methods:

(a) Dry ashing in platinum dishes in an air muffle at temperatures of 450, 600, or 800 °C for a period of 6 hours. The ash was dissolved in 50 ml of 10M HCl and 20 ml of 72% HClO₄, then fumed. The HClO₄ was diluted, 2.5 ml of 9M H₂SO₄ added, and the solution filtered through a No. 41 Whatman paper. The filtrate and residue were analyzed for beryllium by fluorimetry.

(b) Wet ashing in an open 250-ml beaker with 55 ml of 15M HNO₃ and 15 ml of 18M H₂SO₄, as described by Black and Sievers (1). After oxidation was complete, the solution was diluted and filtered. The small siliceous residue was washed, then the paper and precipitate ashed in a platinum dish over a gas burner. The residue was treated with HF + HClO₄, taken to fumes of HClO₄, then diluted. The original filtrate and solution of the residue were analyzed for beryllium.

(c) Wet digestion in a 250-ml flask fitted with a 50-cm reflux condenser, using HNO₃ + H₂SO₄ and the procedure described by Black and Sievers (1). After 4 hr of reflux, the digestion did not appear to be complete; traces of oil could be seen floating on the surface and emulsified with the acids. Additional digestion under reflux gave no improvement, and complete destruction of organic matter was achieved only after the refluxed solution was transferred to a beaker and taken to fumes of H₂SO₄ with occasional additions of HNO₃ to prevent charring. The residual H₂SO₄ was diluted, filtered, and analysed as described in (b).

(d) Wet digestion under complete reflux with a Gorsuch apparatus. An all-glass Gorsuch apparatus (8), consisting of a 250-ml round-bottomed flask, a 50-ml reservoir above the flask, and a 40-cm reflux condenser, was used to achieve complete destruction of the Orchard Leaves under total reflux. A 2-way tap between the flask and reservoir allowed the distillate to either return to the flask, be collected in the reservoir, or be run off to a separate receiver. The Gorsuch apparatus has been used successfully for the wet ashing of volatile complexes of mercury and selenium (8). A 5-gram portion of Orchard Leaves was digested in this apparatus for 4 hr using the same conditions as in (c). A thermometer positioned just above the liquid surface showed that a maximum temperature of 125 °C was reached while refluxing. After 4 hr, the tap was closed so that the nitric acid distillate collected in the reservoir. When all the nitric acid had been distilled from the flask and collected, it was run off into a beaker and reserved for analysis. The temperature was raised until the sulfuric acid fumed and destruction of organic matter was complete. A few small additions of nitric acid were made down the condenser to prevent charring. The small volume of distillate which collected in the reservoir during this final operation was added to the nitric acid previously collected. The nitric and sulfuric acid fractions were then analyzed separately for beryllium.

(e) Wet digestion under complete reflux with a Gorsuch apparatus connected to a Dry Ice cold trap. The experiment described in (d) was repeated, but an all-glass lead-off tube was connected to the top of the reflux condenser via a B29 joint, and led to a 3-cm × 3-cm diam. glass trap immersed in a beaker of powdered Dry Ice. The trap was in position throughout the heating period and, at the end of the experiment, both it and the lead-off tube were rinsed with 6M HNO₃ to dissolve any volatile beryllium compounds collected (1). This solution was analyzed for beryllium along with the two other acid fractions.

Fluorimetric Analysis. Beryllium was determined by the well-known morin fluorimetric method (4, 5). The beryllium acetylacetonate complex was extracted with chloroform in the presence of EDTA to mask interfering metals. After destruction of the beryllium complex by fuming with HNO₃ + HClO₄ + H₂SO₄, the beryllium-morin complex was formed and measured fluorimetrically. A Perkin-Elmer Model 203 fluorescence spectrophotometer was used with an excitation wavelength of 365 nm and an analyz-

er wavelength of 518 nm. The beryllium calibration curve was linear from zero to at least 1 µg Be per 50 ml of final solution. Blanks were carried through the entire analytical procedures. Beryllium spikes were added to 5-gram portions of Orchard Leaves at the start of analysis to determine overall per cent recovery.

Emission Spectrographic Analysis. Emission spectrography was used in an attempt to detect volatile beryllium compounds in Orchard Leaves, and to provide an independent method for the determination of total beryllium content.

In the first series of experiments, samples of Orchard Leaves were arced directly, and compared with beryllium-in-graphite standards (Spex G standards), which contained 0.01 to 1 ppm Be. The spectrographic conditions were as follows: spectrograph, 3.4-m plane grating Ebert (Jarrell-Ash); grating angle, 9.45°; reciprocal linear dispersion, 2.5 Å/mm; slit, 2 × 0.02 mm; gap, 4 mm; source, 10 A dc arc; anode, sample, shallow crater electrode similar to National type L4031; cathode, 60° pointed 6.15-mm diam. rod, National SPK grade; emulsion, Kodak SA3; development, 4 min Kodak D-19, 4-min fix.

In the second series of experiments, 20-mg portions of Orchard Leaves were loaded into the bottom of deep crater electrodes, and a boiler cap (9) fitted. The electrodes had thermocouple leads sealed into the wall just above the charge so that its temperature could be measured during arcing. Two charge temperatures, 400 and 200 °C, were achieved by using 4.75-mm i.d. electrodes which were 19 mm and 35 mm deep, respectively. The samples were arced at 10 A, and moving plate spectra recorded for each 10 sec of a 60-sec exposure, using the same conditions as in the first series of experiments but with a 0.03-mm slit. Any volatile beryllium compounds from the sample would have to emerge through the hole in the boiler cap and enter the plasma. To prove that a volatile beryllium compound would be detected by the boiler cap electrode technique, 20-mg portions of graphite were weighed into the deep crater electrodes and spiked with aliquots of a solution of beryllium acetylacetonate in chloroform. Beryllium was easily detected at both 200 and 400 °C, and a limit of detection of 5×10^{-4} µg Be was estimated. With a 20-mg sample charge, this corresponds to a limit of detection of 0.025 ppm volatile beryllium in the sample.

Gas Chromatography. A 5-gram portion of Orchard Leaves was refluxed for 4 hr with HNO₃ + H₂SO₄ as described by Black and Sievers (1). The solution was diluted to 100-ml, and 10-ml aliquots taken for extraction with Htfa. The extractions were carried out exactly as recommended by Black and Sievers. The Pierce Chemical Co. Htfa was vacuum distilled before use because it was found that the as-received Htfa gave large interfering chromatographic peaks. Pure Be (tfa)₂ was synthesized from the distilled ligand (theor., 2.86% Be; found, 2.76% Be) and solutions of the complex were prepared in benzene in order to calibrate the gas chromatograph. The chromatograph used was a Hewlett-Packard Model 5750 equipped with a ⁶³Ni source electron capture detector. The column, support, stationary phase, and temperatures were identical to those used by Black and Sievers (1), but the carrier gas was 4%, rather than 10%, CH₄ in Ar, with a flow rate of 42 ml/min.

RESULTS AND DISCUSSION

The fluorimetric results, corrected for moisture content determined on a separate sample, are shown in Table I. There was no significant difference between the results obtained using a wide variety of dry ashing and wet ashing procedures. The mean result for acid soluble beryllium of 0.0213 ± 0.0035 ppm Be (1 σ) in NBS Standard Reference Orchard Leaves (dry basis) is similar to the figure of 0.017 ± 0.003 ppm Be found by Black and Sievers when the sample was digested in an open beaker. Our observation that no beryllium is lost by muffle ashing at temperatures as high as 800 °C was not unexpected, because the most likely product of the dry ashing of an organic beryllium compound is the highly refractory oxide, BeO (2). No beryllium was detected in the nitric acid distillates using the Gorsuch apparatus, or in the dry ice trap leading from the condenser.

Emission spectrographic analysis with a shallow crater

(8) T. T. Gorsuch, *Analyst (London)*, **84**, 135 (1959).

(9) G. H. Morrison, Ed., "Trace Analysis," Interscience, New York, N.Y., 1965.

Table I. Beryllium in NBS Orchard Leaves

Ashing procedure	Be in Orchard Leaves, ppm ^{a,b}	Recovery of spike, % ^c
(a) Dry ashing, 450 °C	0.019, 0.019 ^d	101
600 °C	0.017 ^e	
800 °C	0.023, 0.027	
siliceous residue	0.008	
(b) Open beaker, HNO ₃ + H ₂ SO ₄	0.027, 0.025, 0.018, 0.020	94, 95
siliceous residue	0.009, 0.009	
method blank	<0.002 ^f	
(c) Refluxed with HNO ₃ + H ₂ SO ₄	0.019	
for 4 hr, then fumed in open beaker		
(d) Gorsuch apparatus, HNO ₃ + H ₂ SO ₄		
HNO ₃	<0.002	
H ₂ SO ₄	0.020	
(e) Gorsuch apparatus with dry ice trap,		
HNO ₃ + H ₂ SO ₄		
HNO ₃	<0.002, <0.002 ^g	
H ₂ SO ₄	0.021, 0.022 ^g	95
trap	<0.002, <0.002 ^g	

^a Results are for separate 5-gram weighings, and have been corrected for moisture content of 5.9% (24 hr at 90 °C). ^b Results do not include Be in siliceous residue. ^c 0.5 µg Be spike added at start of analysis. ^d Ash = 9.6%. ^e Ash = 7.2%. ^f Limit of detection. ^g These three results were obtained on a second sample of Orchard Leaves received from NBS 6 months after the first sample.

electrode gave a limit of detection of 0.02 ppm Be using graphite standards. No beryllium could be detected in the Orchard Leaves by this technique. To check the unlikely possibility that beryllium compounds were present which were so volatile that they escaped the plasma, the sample was also analyzed using a deep crater electrode fitted with a boiler cap. Again, no beryllium was detected in Orchard Leaves and, by comparison with beryllium acetylacetonate standards, it was concluded that the content of volatile beryllium compounds must be less than 0.025 ppm Be.

Gas chromatographic analysis of pure solutions of Be(tfa)₂ in benzene gave well-defined peaks with a retention time of 4.9 min. However, we were unable to determine beryllium in the Orchard Leaves extracts because of the presence of very large interfering peaks which occurred close to the beryllium peak. These interfering peaks were not present in blanks or standards carried through the same analytical procedure, and appear to result from the extraction of some of the undestroyed organic matter which is still visibly present after prolonged refluxing of Orchard Leaves with nitric and sulfuric acids.

As a result of our fluorimetric and emission spectrographic studies, we have concluded that NBS Standard Reference Orchard Leaves has a total beryllium content (acid soluble + siliceous residue) of 0.030 ± 0.004 ppm Be (dry

basis) and that the sample contains no beryllium compounds which are volatile below 800 °C. Two separate sample bottles of Orchard Leaves, received six months apart, were analyzed for beryllium and no significant difference was found (Table I). The high results obtained in the earlier study (1), and the identification of very volatile beryllium compounds in Orchard Leaves, may have been due to undestroyed organic matter interfering with the gas chromatographic measurement technique.

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Comments on Ratio Matching

Sir: Anders (1) proposed a new statistical method for discovering the generic relationship among samples. Though intuitively appealing, the ratio matching technique for discovering the generic relationship among samples suffers from lack of logic foundation and mathematical consistency. In this paper, the method is reviewed and then criticized. Techniques for analyzing this kind of data are also

suggested.

The method can well be explained by his own example. Suppose we have two sets of sediment samples; one from a Michigan waterway (sample A) and the other from a California waterway (sample B). Each sample consists of concentrations of eight chemical elements As, Sb, Cu, Zn, Au, Cd, Hg, and Cr. The concentration ratios " x_{ij} " for a sample are formed by dividing the concentration of each element by that of some other elements. That is,

(1) O. U. Anders, *Anal. Chem.*, **44**, 1930 (1972).