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NBS/EPA ENERGY ENVIRONMENT PROJECT

SEMI-ANNUAL REPORT
TO
ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF ENERGY, MINERALS, AND INDUSTRY
WASHINGTON, D. C. 20460

JULY 1979

U. S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS
WASHINGTON, D. C. 20234

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Page 10, 1.a.	Should read "Raman Microprobe Characterization of Trace Polynuclear Aromatic Hydrocarbons.
Page 25	Delete title
Page 30, 1.d.	Should read SRM 1643a.

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FOREWORD

The role of the National Bureau of Standards (NBS) in the Interagency Energy/Environment R&D program, coordinated by the Office of Research and Development, U. S. Environmental Protection Agency, is to provide those services necessary to assure data quality in measurements being made by a wide variety of Federal, state, local, and private industry participants in the entire program. The work at NBS is under the direction of the Office of Environmental Measurements and is conducted in the Center for Analytical Chemistry and the Center for Radiation Research. NBS activities are in the Characterization, Measurement, and Monitoring Program category and address data quality assurance needs in the areas of air and water measurement methods, standards, and instrumentation. NBS outputs in support of this program consist of the development and description of new or improved methods of measurement, studies of the feasibility of production of Standard Reference Materials for the calibration of both field and laboratory instruments, and the development of data on the physical and chemical properties of materials of environemntal importance in energy production. This report is one of a series issued every six months by NBS to provide information to the interagency Energy/Environment community on the status of methods, standards and data projects at NBS. Detailed project information is also provided in the Interagency Energy/Environment Resarch and Development Series.

C. C. Gravatt
Chief, Office of Environemntal Measurements
National Bureau of Standards

INTRODUCTION AND SUMMARY

This report describes work performed by the National Bureau of Standards (NBS) during the period, January 1979 to June 1979, under the Interagency Agreement (EPA-IAG-D8-E684) between the U. S. Environmental Protection Agency and NBS. This Agreement covers the development of standards, methods, data, and instrumentation for the measurement of pollutants associated with energy production and use. The highlights for this reporting period in the eight subagreement areas are:

80 BCKa - ENERGY RELATED POLLUTANT MEASUREMENT AND INSTRUMENTATION DEVELOPMENT

Under the task Energy-Related Water Pollutant Analysis Instrumentation for Research and Ambient Characterization Studies, several refinements have been incorporated into the liquid chromatography-mass spectrometry interface, some practical operating experience was gained with the refined system and scientists are developing plans to apply this system to analytical problems.

Studies of organic layers on particles by ion microprobe mass analysis revealed that characteristic fragment ions as well as parent molecule ions can be observed in spectra obtained from layered particles.

Development of the Master Analytical Scheme progressed sufficiently during this reporting period so that three major NBS responsibilities were defined.

Significant progress was made in the electrochemical detection of organometallic compounds by optimizing detectors used in the system and improving the separation of organo species in the liquid chromatography step.

A final report is being prepared on the laser-enhanced ionization work.

80 BCKb - ENERGY RELATED WATER POLLUTANT ANALYSIS INSTRUMENTATION

Under the task Development of Measurement Methods for Non-Volatile Organic Pollutants in Water Due to Energy Technologies work is being performed to optimize the NBS-developed Raman microprobe for its application to the analysis of small volumes of organic effluents.

Work is being performed on the development of specific immunoassays for dinitrophenols in water. Considerable effort has been spent developing a technique to optimize a small molecule immunoassay using tritrated dinitrophenol or a derivative thereof.

Wave guide coherent anti-Stokes Raman Spectrometry has been shown to be a sensitive and highly specific "detector" for trace organics when coupled with chromatographic separation techniques.

80 BCLa - ENERGY RELATED POLLUTANT MEASUREMENT AND INSTRUMENTATION DEVELOPMENT

Under the task, Development of SRM's for Stationary Sources Associated with Energy Production, mixtures of NO_2 in air at 250, 500, 1000, and 2500 ppm were procured for certification and preliminary homogeneity analyses of the 250 and 500 ppm mixtures were completed; two new SRM's for NO in nitrogen at 1500 and 3000 ppm were certified and are now available; and analyses have been initiated for certification of O_2 in nitrogen at 2 and 10% O_2. Under Development of SRM's for Monitoring of Ambient Air Impacted by Emissions Resulting from Energy Production, preliminary work for the preparation of CO_2 in air mixtures in the 100-500 ppm range indicated that a total CO_2 concentration uncertainty of $\pm$ 0.1% relative may be achieveable; a second NBS Computer Operated Gas Analysis System (COGAS) having up to a 30-cylinder capacity is being assembled; and an NBS traceability procedure has been prepared for production of gas standards ("Certified Reference Materials") by the compressed gas suppliers that would provide traceability of commercial gases to NBS.

In X-ray fluorescence particulate analysis, work continued on focused-ion beam sputtering to produce thin glass films. Two additional glass targets of different elemental compositions have been used for thin filter preparation.

Under Particulate Physical and Chemical Composition, the internal calibration of the Particle Doppler Shift Spectrometer was improved by a factor of four for measurement of 5-18 μm aerosol, and prospects are promising to extend the measurements down to 0.5 μm or less. In addition, numerical calculation techniques have been developed for nonspherical particles, and the capability now exists to calculate optical scattering properties of a variety of nonspherical particles as a function of particle shape, size, and index of refraction. Further, work has progressed on evaluation of an air-supported plasma torch, which, when coupled to a laboratory spectrometer and recorder, can be used for direct monitoring of airborne lead (or mercury), the net system of which is readily amenable to minaturization as a portable instrument.

Glass fiber filter strips as candidate SRM's containing nominal concentrations of 100, 300, and 1500 μg of lead per strip were prepared and analyzed by linear sweep voltammetry. Recoveries of lead from these strips for analysis and the precision and accuracy of analysis were all found to be excellent.

NBS SRM 1648, Urban Particulates, collected in the St. Louis area, has been certified for a number of elements and was made available by the NBS Office of Standard Reference Materials in March. Collection of urban air particulate matter in the Washington, D. C. area has progressed well. Preliminary analyses have been carried out on the Washington collection for inorganic and organic components, and comparisons have been made to the St. Louis material.

Under SRM development for coal conversion processes, Western Coal (SRM 1635) was found to contain about 18 times more low evaporation temperature sulfur than Pennsylvania Coal (SRM 1632a). Preliminary analyses were completed for organic surface layers on single particles using a differential backscattering system.

Under activities on oil shale, preliminary analyses were undertaken for organics extracted from an homogenized oil shale using gas chromatography and glass capillary columns.

80 BCLb--ENERGY RELATED AIR POLLUTANT ANALYSIS INSTRUMENTATION

A systematic study of the effects of SO_2 concentration and relative humidity on response of the Particulate Sulfate Instrument found that the flame photometric detector was sensitive to sample relative humidity only below 10% and above 80%, and that SO_2 interferred with the particle sulfate response only at very high SO_2 concentrations.

80 BCLc-ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

Work on the mini-radiocarbon low-level counting method and instrumentation, focusing on the use of radiocarbon as an environmental tracer to discern natural from anthropogenic carbon sources, demonstrated the validity of the method in the field and served to underline the potential serious impact of residential wood burning on fine carbonaceous air particulates in urban areas.

80 BCMa - ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

Under the Energy Related Water Pollutant Standards Reference Materials for Conventional Fossil Technology task, the Trace Elements in Water SRM (1643a) is in the final stages of certification and will soon become available. There was no activity this reporting period on the ocean sediment SRM, Estuarine Sediment SRM or on the Anion SRM.

Work on the Inductively Coupled Plasma (ICP) technique focused on isolation and optimization of non-random variability in the measurement technique. Some progress has been made. Additionally, a continuum-source Echelle wavelength modulation-atomic absorption spectrometer (CEWM-AA) is being evaluated for the determination of trace metals in a wide variety of samples.

In the area of SRM's for organic analysis, the procurement process for the production of an aqueous PAH-SRM is still in progress. Additionally, NBS is participating in an interlaboratory comparison exercise to both validate NBS general methodology and check the effect of refinements to this methodology.

A new measurement technique--laser Raman scattering in isolated cryogenic matrices--is being investigated for the analysis and certification of priority pollutants in materials.

80 BCMb - ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

The work under this task is focused on the development of Standard Reference Materials (SRM's) for organic water pollutants associated with emerging energy technologies. Current measurement methodology is not adequate for the development of SRM's required to support effective monitoring programs for advanced energy-related organic water pollutants. Thus, efforts are closely related to BCKb elements.

80 BCN - ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

The work in the Radiological Pollutant Quality Assurance task involved providing measurement traceability, through the EPA/Las Vegas Laboratory, for certain radionuclides not included in other programs. Efforts were focused on providing four materials to be used in a radiological pollutant quality assurance program: Plutonium-241 solution; thorium-232 solution; fly ash from coal combustion; and a mixed radionuclide solution.

80-BCK-a-ENERGY RELATED POLLUTANT MEASUREMENT AND INSTRUMENTATION AND DEVELOPMENT

1. Energy-Related Water Pollutant Analysis Instrumentation

1.a. Development of Marker Compounds

Development of the Master Analytical Scheme has progressed sufficiently that the following NBS responsibilities have been defined.

1) NBS will synthesize a deuterium labeled naphthalene sulfonic acid and labeled disodiumdodecyl phosphate. If a synthetic route cannot be found, NBS will report their research results by the end of August 1979.

2) NBS will perform purity checks on the approximately forty deuterated marker compounds to be supplied by Research Triangle Institute and Gulf South Research Institute. These purity checks will include checks for isotopic as well as chemical purity of the marker compounds. The target date for supplying this information will be 30 days after receipt of the samples.

3) Once marker compound solutions for the Master Analytical Scheme can be prepared, NBS will monitor stability of these solutions for the duration of the Master Analytical Scheme contract (i.e., through the end of phase three). Included in the stability monitoring will be reactivity of the components in the mixture and long-term losses of components of the mixture for other reasons. The stability of these solutions will be monitored both at refrigerator and at room temperatures.

1.b. Application of Selective Detectors to Liquid Chromatography

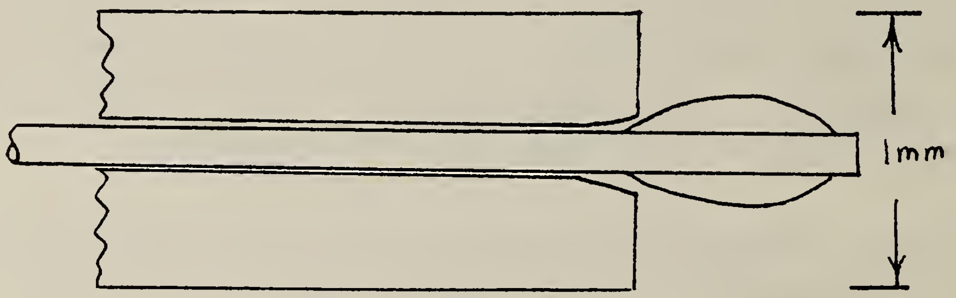
See section BCK-a-1.e.

1.c Liquid Chromatography-Mass Spectrometry

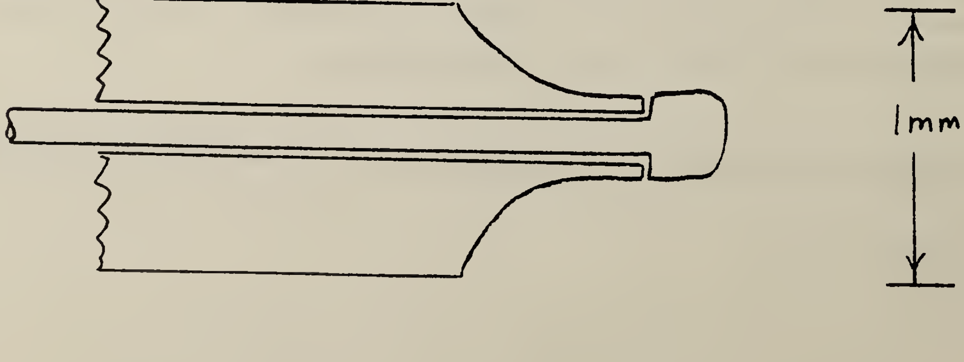
Several further refinements have been incorporated into the LC-MS interface and some practical operating experience has been gained during this reporting period. Heaters composed of Chromel wire with bases cast of refractory cement were designed and fitted to the ion source. The heaters make it possible to achieve source temperatures of above 350 °C, if desired, and to maintain the source temperature while the filaments are off.

The probe was fitted with an improved heat sink which is vented so as to prevent the interior of the heat sink from being a dead volume connected to the ion source.

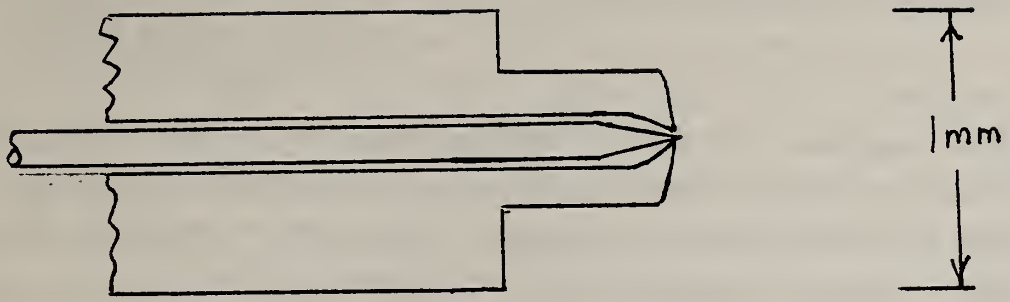
It was discovered that the probe valve configuration was not giving a spray of liquid. Therefore the probe valve was changed from:



to



and finally to:



Tests showed that the latter configuration gave the desired spray of liquid. A thermocouple device was constructed to measure the temperature at the probe tip; the temperature appears to not exceed 35 °C when in the desired position.

The mass spectrometer was tuned with perfluorotributylamine, good resolution being obtained. The detection limit of methyl stearate on the solids probe was measured to be about 1 ng.

Two liquid chromatographic separations were monitored with the mass psectrometer. A mixture of polynuclear aromatic hydrocarbons (PAH) was eluted from an aminosilane column with i-octane containing 5 percent methylene chloride at a flow rate of 1 mL/min. The elutent was passed through a UV detector, doe the concentrator wire, and into the mass spectrometer. The peaks were about 30 seconds wide at the UV detector and were delayed about 1 minute and broadened by about 15 seconds at the mass spectrometer. The detection limit for phenanthrene, for example, was found to be about 2 ng injected into the column. Without the use of the concentrator wire, the detection limit was about 40 ng.

A mixture of aromatic nitrogen compounds was examined, injecting 200 ng of each and eluting with i-octane containing up to 20 percent methylene chloride. It was found that, by varying the flow rate of solution into the source, spectra of Chemical Ionization or mixed Election Impact Chemical Ionization character could be obtained.

A control device for the power input to the concentrator wire was constructed. It operates on the principle of monitoring the drop size at the bottom of the wire with a photocell feedback circuit controlling the applied current. This allows us to approach very nearly zero flow at the bottom of the wire without overheating and depositing the solute on the wire. Approximate maximum LC flow rates which can be accommodated are shown in Table 1.

Table 1

Solvent	Max. Flow Rate, mL/min	ΔHv cal/g
n-pentane	3.1	90
i-octane	2.8	90
methanol	1.7	280
50% MeOH/H_2O	0.7	420

A limitation in the amount of concentration increase which can be obtained is the loss by capillary migration of solution from the junction of the concentrator wire and the point of entry into the probe tube. Teflon FEP coatings and PTFE bushings have been tried with only moderate success. A change in the geometry may be necessary.

Further development of the power control of the concentrator will eventually be necessary, as will the trial of several means to prevent loss of solution from the junction of the concentrator wire and the probe tube. Apart from the above, we are now at a point in the development of the LC/MS interface where we can begin to apply it to analytical problems.

A patent application has been filed with the NBS legal advisor and he has been in contact with the appropriate EPA counsel, Mr. Ben Bochenek.

1.d Feasibility Study of Application of Ion Microprobe Particulate Analysis

The project on the investigation of organic layers on particles by ion microprobe mass analysis has been initiated and work is now in progress. We are currently studying known organic layers deposited on metallic spheres. The initial studies have revealed that characteristic fragment ions as well as parent molecule ions can be observed in spectra obtained from layered particles in the 20-25 μm range. Additional studies will be carried out, and a final report on the project will be available in September 1979.

1.e Liquid Chromatography with Electrochemical Detection of Organometallic Compounds

Significant progress has been made in the electrochemical detection of organometals and organic compounds separated by LC. The work has been divided between detector optimization and species separation.

Detector Optimization

Various electrode materials were evaluated for their use in reductive electrochemical detection. Six electrodes including the dropping and hanging mercury, gold amalgam, platinum amalgam, glassy carbon and mercury coated glassy carbon electrodes were compared for their potential ranges and detection limits for a reducible organic compound. A manuscript detailing this work has been submitted to Analytical Chemistry.

Organotin Separation and Detection

Some of the trialkyl organotin cations have been separated by reverse-phase chromatography using an organotin complexing agent with dimethylsulfoxide (DMSO). Organotins most frequently behave as "hard" Lewis acids, and DMSO was chosen as a suitable "hard" Lewis base. Together they form neutral complexes of the type $R_3Sn(DMSO)_x$ (counter anion), where X can be 1 or 2 (1). The neutral complexes are then separated by reverse-phase chromatography (see Figure 1).

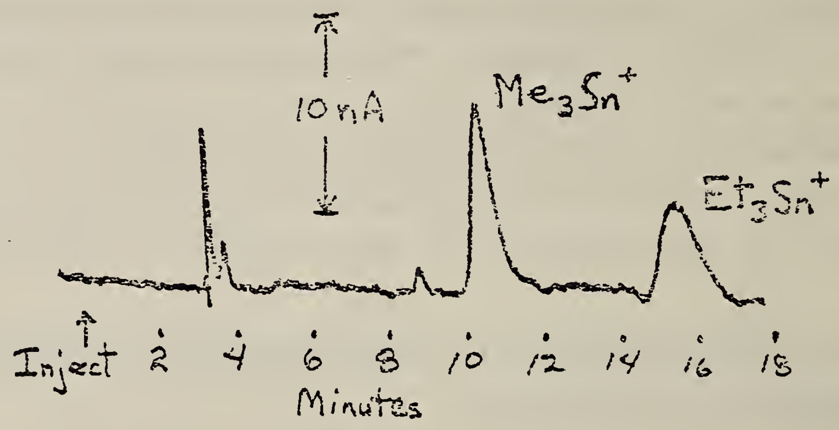


Figure 1

A cation exchange separation has been developed by Jewett et al. (2,3) for the trisubstituted organotin cations. This separation was used for further evaluation of the electrochemical detection approach, outlined in the following text.

Some difficulty has been encountered when constant potential amperometry is employed for the detection of the organotin cations. Figure 2A shows the amperometric detection of ϕ_3Sn^+ at a potential that produces a current on the limiting current plateau. A positive reduction current due to the ϕ_3Sn^+ is initially observed, followed by a significant dip in the residual current baseline. This behavior can be explained by the electrochemical behavior of the trisubstituted organotin cations:

$$\phi_3Sn^+ + e \overset{\sim -0.7\ V}{\rightleftarrows} \phi_3Sn\cdot\ (ads) \quad \text{I}$$

$$2\phi_3Sn\cdot\ (ads) \xrightarrow{\text{slow}} \phi_6Sn_2 \quad \text{II}$$

The ϕ_3Sn^+ is initially reduced quasi reversibly to the $\phi_3Sn\cdot$ radical which is adsorbed at the electrode surface (4). If a constant potential is applied just above -0.7 V, sufficient $\phi_3Sn\cdot$ is produced to dimerize (II). The ϕ_6Sn_2 produced is highly adsorbed at the electrode surface and is not further reducible at this applied potential. The ϕ_6Sn_2 covers the electroactive surface of the electrode, which lowers the residual baseline current (caused by the solvent), resulting in the observed dip.

This detection problem can be overcome by using a pulsed waveform rather than holding the constant potential above -0.7 V. Figure 2B illustrates the approach, where a potential is applied which does not cause (I) but periodically a more negative potential pulse is applied which does initiate reaction I. The reduction current is sampled at the end of the pulse, still giving a response proportional to the ϕ_3Sn^+ concentration, but now the duty cycle of the electrode is greatly reduced (to 10% in Figure 2B and C). Therefore less $\phi_3Sn\cdot$ is generated. During the main duration of the potential cycle the $\phi_3Sn\cdot$ produced can also be reoxidized to ϕ_3Sn^+ by the return to a more oxidizing potential. The low duty cycle and reoxidation prevents the buildup of ϕ_6Sn_2 and therefore eliminates the baseline dip. Even higher sensitivity can be obtained if the differential pulse mode of operation is employed (shown in Figure 2C).

The differential pulse mode of detection was used for the measurement of very small amounts of two trialkyltin species shown in Figure 3, by using a compromise detector potential and large pulse height (potential window). A somewhat better detection limit could be obtained if the potential and pulse height were optimized for each species.

Future work will involve development of a separation of the mono- and disubstituted tin species and an investigation into the water stability of the dialkyltin cations.

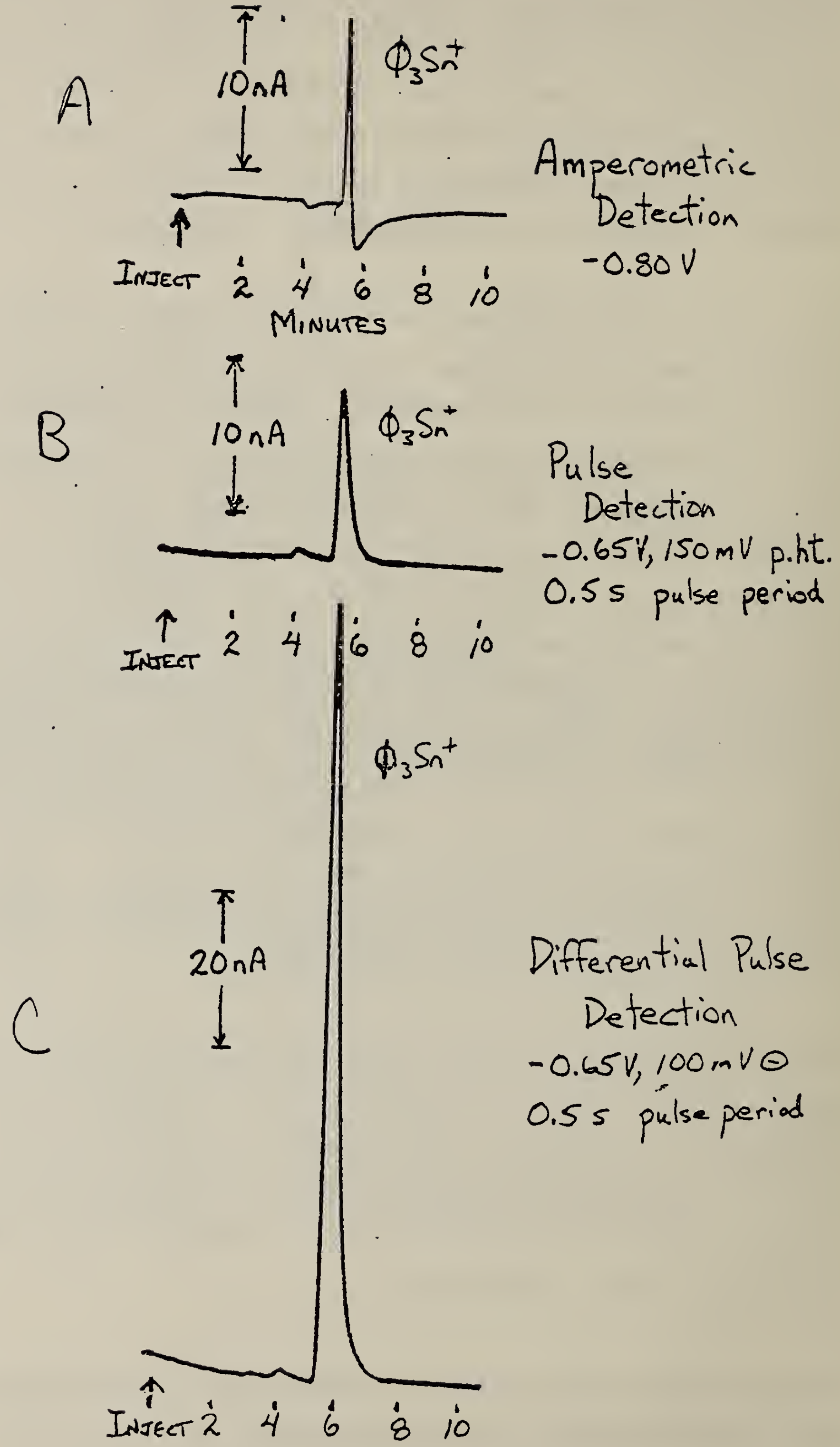

A
10nA
Φ_3Sn^+
Amperometric Detection
-0.80 V
INJECT
2
4
6
8
10
MINUTES
B
10nA
Φ_3Sn^+
Pulse Detection
-0.65V, 150mV p.ht.
0.5 s pulse period
INJECT
2
4
6
8
10
Φ_3Sn^+
C
20nA
Differential Pulse Detection
-0.65V, 100mV ⊖
0.5 s pulse period
INJECT
2
4
6
8
10

FIGURE 2

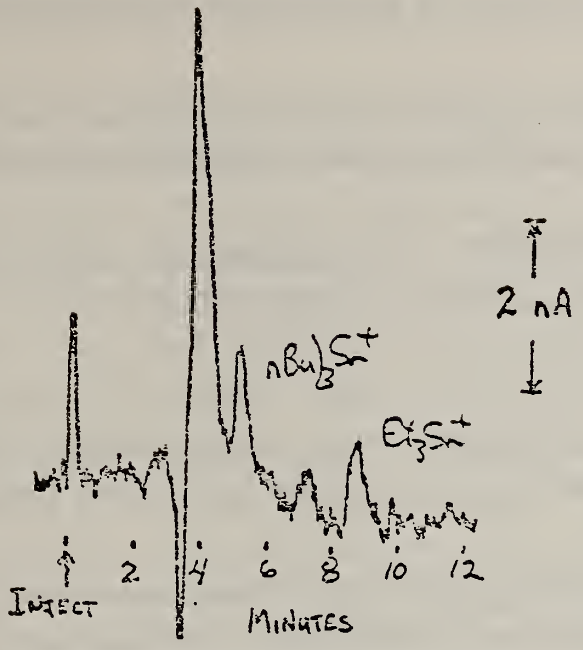


Figure 3

References

1. R. C. Poller, Chemistry of Organotin Compounds, Academic Press, N.Y., 1970.
2. Speciation of Triorganotin Halides by HPLC-GFAA, K. L.Jewett, F. E. Brinckman, and W. R. Blair, 186th ACS Natl. Mtg., Washington, D. C., September 1979 (Analytical Div).
3. New Methods for Speciation of Bioactive Organotin Leachates from Antifouling Paints and Polymers, K. L. Jewett, W. R. Blair, and F. E. Brinckman, 6th International Symposium on Controlled Release of Bioactive Materials, New Orleans, LA, 6-8 August 1979.
4. S. G. Maironovskii, Russ. Chem. Rev. 45, 298 (1976).

1.f Laser Enhanced Ionization

A final report is being prepared on this activity.

80-BCK-b-ENERGY RELATED WATER POLLUTANT ANALYSIS INSTRUMENTATION

1. Development of Measurement Methods for Non-Volatile Organic Pollutants in Water Due to Energy Technologies

1.a. Raman Microprobe Characterization of Trace Polynuclear Polynuclear Aromatic Hydrocarbons

Activities have recently been resumed in the project area. The analytical goals and the status of this work as of two months ago are described in a recently published paper (1).

It was demonstrated that micro-Raman spectroscopy (MRS) offers high molecular/structural specificity and picogram sensitivity for PAHs of interest in environmental pollution studies. Based on the results of feasibility experiments, it was proposed that the MRS technique be developed as a potentially powerful, new method for the detection and identification of trace level organics separated by chromatographic procedures.

The work that has now been initiated aims at applying the NBS-developed Raman microprobe to the analysis of isolated, small volumes of the effluent from a liquid chromatograph. Because of the design of the instrument (i.e., the illumination/collection geometry utilized in the fore-optical system), it is necessary that any desired fraction of the chromatographic effluent stream be isolated and analyzed in a static mode. This requires that fractions of the effluent be trapped and localized on a sample support which does not interfere with the microprobe measurement. Various schemes are being investigated for the collection and localization of liquid chromatographic fractions. Isolation in microscopically confined areas (or sampling volumes) of sapphire substrates has particular advantages in that sapphire (α-Al_2O_3) presents only minimal spectral interferences by Raman (and fluorescence) scattering (1). A second approach isolates the effluent by adsorption onto a fine particulate solid (e.g., alumina) which can be analyzed in the microprobe by the usual techniques.

1.b. Development of Specific Immunoassays for Dinitrophenols in Water

Work during the past six months has focused on the techniques required to optimize a small molecule immunoassay using tritiated dinitrophenol or the tritiated derivative. Dinitrophenol-L-lysine, ε-[phenyl 1,3,5-^{3}H(N)]. Charcoal and several types of antibody-coated beads were used as separating agents.

Results obtained so far showed that only a small fraction of the H^3-DNP-Lys is bound (ca. 1% or less at about 1 μg/mL of the antigen); and the precision is still rather poor. It appears that there are significant non-specific binding reactions and that the affinity of the antibody for DNP-Lys is not as strong and specific as we had hoped. We tried various procedures to eliminate some of the sources of variability in the results and, hopefully, to be able to still obtain an immunoassay for DNP with the material currently available.

(a) Purification of the Antiserum by Affinity Column Chromatography

The majority of the albumin and non-antibody protein in the serum is removed by use of DEAE cellulose (D52) columns and then by an affinity column packed with affi-gel 102 reacted with EDNP-lysine. The antibody fractions were dialyzed in an ultrafiltration cell and analyzed by means of cellulose acetate electrophoresis. The purified material showed only marginal improvement over the antiserum specificity and affinity toward the EDNP-lysine. Further work is indicated here since the antibody appears to be very pure.

(b) Charcoal precipitation

Darco charcoal was used to precipitate out all unbound antigen from the solution. Only the bound antigens are supposed to remain in the solution phase. However, we found that in the solutions without any antibody, a residual activity remains in the solution after the charcoal precipitation. The magnitude of this residual activity is of the same order as the activity in the supernate when antibody is present. Thus the correction for the background count is as large as the net count for bound antigen. Increasing the charcoal to fourfold the normal amount employed did not decrease this background count significantly. Work indicates the need to use solid-phase beads coated with a second antibody as a means of separating the free from the bound antigen.

(c) Immunobeads

We had tried several of the commercially available beads, e.g., DASP, which is a sheep anti(rabbit immuno-globulin) immunosorbent, and immunobeads of Bio-Rad, which are beads with rabbit IGG bound to them. In these techniques, the bound DNP-lysine is precipitated with the beads, therefore the activity of the precipitate is only a small fraction (ca. 1%) of that in the supernate, because of the low affinity of the antibody. The precipitates have to be washed at least twice, with about 10-fold the volume of the precipitate. However, excessive washing seems to increase the variability of the results, probably due to either the loss of beads or the shift in binding during washings. Due to the configuration of the polyethylene vials we normally used, the precipitates were not packed well, and the precision suffered because of inclusion of supernate and loss of some of the beads during washing and removing of the supernatants. We subsequently tried a narrower glass tube with rounded bottom, and the reproducibility of assay improved. However, the adsorption of the antigen onto the surface of these tubes gives a background count comparable in magnitude to the net count from the beads.

The low affinity and specificity of the available antibodies seem to be limiting the development of a sensitive and accurate RIA. Most of our results at present are qualitative. Preliminary results indicate that competitive binding of non-radioactive DNP-Lys appears to lower the count of the bound radioactive DNP-Lys in the precipitates. However, due to the large background count at present, we are not able yet to quantitate the results to obtain a standard curve. It appears that we might beneficially spend some effort in obtaining an antibody which has stronger affinity toward DNP, thus making the interferences and errors due to the background relatively insignificant.

Other approaches will include the potential use of labeling the antibodies with iodine-125 in an attempt to utilize the more specific procedure of antibody labeling with a high specific activity gamma emitter.

A variety of DNP-labeled compounds have been procured in the past few months. These compounds are expected to show fluorescence quenching and spectral shifts in the presence of specific antibody. Work will be directed toward this phase of the project during June and July, 1979.

1.c. <u>LC-MS</u>, Covered under Section 80-BCK-a,1.c.

1.d. <u>LC-EC</u>, Covered under Section 80-BCK-a,1.e.

1.e. <u>Ion-Probe</u> - Covered under Section 80-BCK-a,1.d.

1.f. <u>Generation of Enhanced CARS Spectra of Organic Liquids in Capillary Waveguides</u>

NBS scientists have demonstrated the generation of coherent anti-Stokes Raman spectra (CARS) in a liquid filled optical wave guide. This is the first demonstration of the ability of an optical wave guide to produce, over a substantial portion of its total length, frequency tunable, phase matched non-linear mixing in a dispersive medium. Non-linear mixing in a dispersive medium requires fixed angular crossing of the interacting beams (momentum conservation), and thus, these results demonstrate that the wave guide maintains the necessary angular relationships over a substantial fraction of its length. The wave guide technique leads to CARS signals 1-2 orders of magnitude stronger than those obtained by more conventional CARS techniues. This signal enhancement is realized for samples whose total volume is only a fraction of a microliter (total volume of the wave guide is $\tilde{-}0.75$ μL). In the wave guide, signal is generated from virtually all this volume, which should be contrasted with conventional methods which effectively utilize only a few hundred picoliters of a sample whose total volume is tens of microliters (at minimum). Wave guide CARS is particularly significant for analyzing small volume such as the eluent from a liquid chromatograph. A simple hollow quartz or Pyrex capillary, as used in these experiments, is well suited for this application. CARS has been shown to be a sensitive and highly specific "detector" for trace organic analysis when coupled with chromatographic separation techniques.

The inherent efficiency of optical excitation within a wave guide, and the enhanced sensitivity of vibrational spectroscopy by wave guide CARS suggests this as a potentially important tool for studying excited state dynamics in liquids.

Reference

[1] E. S. Etz, S. A. Wise, and K. F. J. Heinrich, "On the Analytical Potential of Micro-Raman Spectroscopy in the Trace Characterization of Polynuclear Aromatic Hydrocarbons," in Trace Organic Analysis: A New Frontier in Analytical Chemistry, Proc. 9th Materials Research Symposium, NBS Special Publication 519, U. S. Government Printing Office, Washington, DC (April 1979).

80-BCL-a-ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

1. Development of SRMs for Stationary Sources Associated With Energy Production

1.a. NO_2 in Air Gas Blend SRMs

The NO_2-air mixtures at 250, 500, 1000 and 2500 ppm have all been ordered in lots of 52 each. The 250 and 2500 ppm mixtures were received in early June after a long delay due to technical difficulties encountered by the gas supplier. The 500 and 1000 ppm mixtures are scheduled for delivery around mid-July.

The cylinders are expected to have a relatively wide range of concentration within each batch when compared to other less reactive gas mixtures prepared in the same manner. However, the stability is expected to be satisfactory. Continuing analyses of 500 and 2500 ppm mixtures over the past 2 years have shown no essential instability.

Three methods of analysis will be employed in the certification of these materials as SRMs. The concentration of each sample in a lot relative to all others in the lot will be determined by chemiluminescence. The absolute value of a limited number of samples will be determined by a chemical method, following an accurate dilution of the sample, and by a gravimetric technique. These two methods have been intercompared and were found to agree to better than ± 1% relative.

The analysis of these samples is considered of highest priority because of the necessity for a second analysis at some later date of at least a portion of each batch. This is considered essential to establish the stability of the commercially-prepared samples.

1.b. SO_2 in Air SRMs

No work was done during this reporting period due to lack of funds for purchase of SRMs.

1.c. NO in N_2 SRMs

Two new SRMs have recently been developed and issued through the NBS-MVMA Research Associate Program. These are SRM numbers 2630 and 2631 (1500 and 3000 ppm NO in N_2, respectively).

1.d. O_2 in N_2 SRMs

Oxygen in N_2 mixtures at 2 and 10% O_2 have been ordered and delivery is scheduled for mid-July. Appropriate standards have been prepared and the methods of analysis are perfected such that no problems are anticipated with the analysis and certification of these materials as SRMs.

1.e. Stationary Source Gas SRMs

The final report on this phase of the program will be issued by September 30, 1979.

2. Development of SRMs for the Monitoring of Ambient Air Impacted By Emissions Resulting from Energy Production

2.a. Trace Level Reactive Gas SRMs

The preparation of samples SO_2, NO_2 and NO in Air or N_2 at sub-ppm levels as SRMs has been found intractable, and further work will not be undertaken at this time.

2.b. CO_2 in Air

A gravimetric technique has been developed for the preparation of gas mixtures in the range from 100 to 500 ppm. The method allows direct preparation at these levels without the requirement of intermediate steps. Preliminary results using CO_2 and air indicate that a total uncertainty of less than ± 0.1% relative may be readily achieved.

A comparison of several mixtures prepared by this method with those of two other laboratories using different techniques has shown very promising results. A more extensive program supported in part by other agencies is planned to complete the investigation. It is still anticipated that SRMs of CO_2 in air certified with a total error of no more than ± 0.3 ppm will be produced during 1980.

2.c. Automation of Gas Analysis

Work is continuing to expand the capability of the NBS-developed Computer Operated Gas Analysis System (COGAS). However, rather than expanding the capacity from 20 to 50 cylinders it was decided to build a duplicate system having up to a 30 cylinder capacity. It was felt that while another system would cost slightly more than expanding the original system, the increased versatility relative to SRM production would be considerably more cost-effective. Parts for assembly of this second system have been ordered. In addition, a system for automating the calibration of permeation tubes is nearing the point where testing can begin.

2.d. Development of a Traceability Procedure for Gas Standards

The serious shortage of certain gas SRMs has been of great concern to NBS for the past several years. Efforts are underway to increase the number of samples restocked next year, but it is obvious that such an increase will only serve to partially resolve the problem. The continued demand for existing SRMs and the need to produce new ones will continue to occupy a significant percentage of available manpower and require a major portion of the funds available for certification of SRMs.

Accordingly, a procedure has been developed by which the specialty gas industry may produce gas mixtures of SRM quality. These mixtures, tentatively called "Certified Reference Materials" CRMs), will be prepared according to a procedure developed by NBS. Such mixtures will duplicate certain SRMs, and when properly prepared will have total uncertainties slightly greater than the uncertainty of the corresponding SRM. This procedure is currently being reviewed by NBS and by several groups within EPA.

After these reviews are completed, the procedure will be reviewed by representatives of the Compressed Gas Association in order that a full understanding of the procedure and its implications will be attained by those companies who wish to produce CRMs.

3. Develop Methods for Dispersal of Particulates on Filter Media and Methods for Determining and Controlling the Composition and Morphology of Such Dispersed Particulates

Thin Glass Films Produced by Focused-ion Beam Sputtering

In our last semi-annual report (EPA-IAG-08-E684) of February 1979 we described our work on thin glass films produced by focused-ion beam sputtering for calibration of x-ray fluorescence spectrometers. We have recently fabricated two additional glass targets of different elemental composition for use in preparing thin films. One of these consists of SiO_2, Na_2SO_4, and Ma_2O; the other contains Al_2O_3 and Na_3PO_4. Experiments to produce thin foils containing sulfur and phosphorous from these glass targets are now in progress and will be reported in the next semi-annual report.

4. Particulate Physical and Chemical Characterization

4.a. Paricle Doppler Shift Spectrometer (PDSS)

During the last 6 months, the internal calibration of the PDSS has been improved by a factor of four so that the maximum expected error in a 5 to 18 μm diameter dioctylphthalate aerosol measurement is ± 0.05 μm.

Much of the 0.2 μm error mentioned in the last report turned out to be due to an air flow effect which occurs when the entire horizontal cross-section of the chamber surrounding the scattering region is not homogeneously filled with aerosol. This filling condition had not been met by most chamber designs used up to this time.

Effects due to temperature gradients and chamber walls were shown by theoretical and experimental studies to be insignificant. The fact that air flow velocities as small as 0.004 cm/s can be measured illustrates the capability of the PDSS to detect systematic errors affecting size measurements. Our work has uniquely demonstrated the measurement of air flow induced by individual small (5 to 20 μm) particles.

We believe that the size measurement capability of the PDSS can be extended down to 0.5 μm or below by taking advantage of the increase in settling velocity in a partial vacuum due to slip. Since January, we have designed and installed a vacuum system for use in conjunction with the PDSS. Experiments to measure the slip correction to the settling velocity, as well as diffusion by Brownian motion at atmospheric to a few torr pressure, will start soon.

4.b. Nonspherical Particles

Numerical calculation techniques have been developed to predict the optical scattering properties of nonspherical particles. These programs have been developed by modification of several techniques which have appeared in the literature in the last two years. NBS now has the capability to calculate the optical scattering properties of a variety of nonspherical particles, as a function of particle shape, size and index of refraction.

This calculation will be used to evaluate the performance of light scattering particle sizing instruments when they are measuring nonspherical particles, and will be applied to several light scattering instruments such as the forward-angle-ratio-light scattering particle sizing instrument. In addition, we have theoretically evaluated several optical techniques for the detection and identification of nonsherical particles. Work will continue in these areas during the next reporting period and a more detailed report will be provided at that time.

4.d.e. Development of Air Supported Plasmas

The air plasma torch is especially feasible for use in direct monitoring of airborne heavy metals since air serves simultaneously as the sample and plasma gas. If air contains any heavy metals, these heavy metals will be excited by the plasma flame and will emit the spectrum characteristic of the element in the air. This emission can be recorded by using a suitable spectrometer and recorder. The peak heights of the chart output are directly proportional to the concentrations of the elements in the sample. The detection limits for Hg and Pb, using a laboratory unit for direct monitoring of airborne samples, are 30 $\mu g/m^3$ and 20 $\mu g/m^3$, respectively.

In addition, the air plasma direct monitoring system can be produced as a small portable unit. Development of the air supported plasma torch has reached a point where construction of a portable instrument for direct monitoring of heavy metals, particularly Pb in air, can be seriously considered. The torch and its associated electronics can be miniaturized to a degree which will make a truly protable monitor for Pb concentrations (and probably also for Hg concentrations) in ambient air.

5. Particulates on Glass Fiber Filters

Pb in Filter Strips for Monitoring Ambient Air Quality

The need for monitoring the lead particulate content of ambient air has been accompanied by the need for accurate standards and methods of analysis. A proposed SRM for lead on micro-quartz glass fiber strips at three dose levels were prepared in nominal concentrations of 100, 300, and 1500 μg per strip, and analyzed by linear sweep voltammetry. A tentative reference method has been proposed by EPA for analysis of these materials by atomic absorption (AAS). However, the proposed AAS method may be subject to a bias of undetermined magnitude by undissolved solids from the glass filter matrix. Voltammetry, being free of this type interference, was selected as an alternate method of analysis to provide data in support of certification. Although a reference procedure completely different from the method proposed for AAS would have been more suitable, an effort was made to follow the AAS procedure as closely as possible.

Concentration results for the proposed materials are summarized in Table 2. Residual lead in four of the analyzed filters was determined after extraction from the filters (by re-leaching and sonifying with dilute nitric acid). The amount of residual lead found was less than 1 μg/strip for all of the filters re-analyzed, indicating excellent recoveries.

Before final certification of the proposed materials can be completed, the effect of undissolved solids from the glass filter matrix on AAS analysis must be determined.

The necessary measurements to make this assessment will be made during the next reporting period.

Table 2

Lead in Glass Fiber Strips

	Std. A.	Std. B	Std. C
Mean (μg/strip)	99.7	302.9	1505.2
n	26	28	28
Std. Dev. (μg/strip)	1.6	5.4	12.7
Rel. Std. Dev.	1.6%	1.8%	0.8%

6. Urban Air Particulate, Washington, DC Sample

NBS SRM 1648, Urban Air Particulate Matter, collected in the St. Louis area, has been certified for a number of elements and has been available since March of 1979. A copy of the certificate for this SRM was published in the last semi-annual report.

The collection of the Washington, DC Urban Particulate Sample was initiated approximately two years ago. During the summer of 1978 several bags were removed from the collection facility to estimate the amount of material collected and to perform preliminary inorganic and organic analyses. During the summer of 1979, a similar study was conducted. Based on these two evaluations, it now appears that by September or October of 1979, approximately 40 pounds of urban particulate materials will have been collected in the Washington sampling program. It is felt that this is a sufficient amount of material and thus the facility will be shut down, the bags removed, and the particulate matter collected from the bags during the fall of 1979.

Preliminary inorganic and organic analyses of the material in the Washington sample indicates that the inorganic composition is different but not in any major way from that collected in St. Louis. The organic composition of the Washington material appears to be about a factor of 2 greater than that in the St. Louis collection, but this difference may be due to the age of the sample and the method of sample preparation prior to analysis, which was far more extensive for the St. Louis collection than was done for this trial sample for the Washington collection. Based on the preliminary analysis, it appears that the Washington sample can be used in two ways. It can be retained as a second sample to be made available after the sale of the St. Louis material. Alternatively, the Washington sample could be issued as an organic-urban-air-particulate characterized only for its organic composition and provided in sufficient quantity to be used as a standard for organic analysis. Ultimate determination of the use of the material and the nature of its characterization will have to be made after the sample is removed from the bags, and a more detailed preliminary analysis has been completed. This determination should be made in time for the next semi-annual report.

7. Develop SRMs for Coal Conversion Processes and Materials Balance Determinations

Three sulfur species in coal have been reported, pyritic sulfur (FeS_2), sulfate sulfur ($FeSO_4$) and organic sulfur. In these experiments, sulfur and iron emission intensity versus temperature curve were monitored. The method used in this work is based on the detection of differences in vaporization of various chemical species at atmospheric pressure, using plasma emission spectrometry to detect the vaporized element. From the experiments four sulfur species, FeS_2, $FeSO_4$, organic sulfur and low evaporation temperature sulfur were observed. The low temperature species starts to evaporate at approximately 28 °C. Western Coal (SRM 1635) has been found to contain about 18 times more of the low temperature species than Pennsylvania Coal (SRM 1632a). In the future measurements will be made using two monochromators simultaneously to detect the sulfur and iron or other combination of elements.

A preliminary analysis has been performed on techniques which might be used in analyzing organic surface layers on coal-conversion particulates. The two techniques investigated were the micro-Raman technique, and a proposed technique of differential backscattering from single particles. The effectiveness of the micro-Raman technique in analyzing surface layers on single particles is still under investigation and preliminary results of this investigation were presented in the last semi-annual report and are contained in BCKa and b of this report.

The differential backscattering technique has been studied by optical scattering, theoretical calculations to predict the effectiveness of detecting and identifying organic layers on single particulates. Preliminary analysis of this technique indicates that it would be worthy of further experimental evaluation and an investigation of this type is planned for the next semi-annual period. The instrumentation to be used in this analysis is similar to the micro-Raman optical system, but used in a configuration such that the total backscattered intensity from a particle is collected as a function of the incident wavelength. An absorption spectra of the particle, detected by backscattered intensities, is obtained. The major optical noise component in this technique is the specular backscattering from the substrate and the possibility of measuring a signal in the presence of this background can only be evaluated by experimental techniques, which will be reported in the next semi-annual report.

8. Development of an Oil Shale SRM

Samples of an homogenized oil shale material were supplied by T. Gills of the Inorganic Analytical Research Division. One of these samples was Co^{60}-irradiated, the other was not. Twenty grams of each material were separately extracted with 50 mL of methylene chloride and the extracts evaporated to 100 μL. Both concentrates were analyzed by gas chromatography using high resolution glass capillary columns and visually identical chromatograms were obtained. Thus the potential exists for a combined organic/inorganic SRM once organic certification methods are available.

Development of an Oil Shale SRM

A quantity of Oil Shale SRM has been sterilized and set aside for comparison with unsterilized oil shale to determined if there are any changes in the concentration of volatile substances, both organic and inorganic. There has been no further activity in this project to determined the loss of volatile inorganic constituents during the past six months.

80-BCL-b-ENERGY RELATED AIR POLLUTANT ANALYSIS INSTRUMENTATION

1. Development of an Instrument to Measure Airborne Sulfate Particulate Matter

The objective of the Particulate Sulfate Instrumentation project was to develop and evaluate a measurement system having ambient particulate sulfur level detection sensitivity (-0.5 $\mu g\ S/m^3$) and real time response suitable for mobile laboratory and aircraft monitoring applications. The system configuration chosen for development consists of a Flame Photometric Detector (FPD) for measuring total sulfur preceeded by a pulsed electrostatic precipitator which modulates the particulate concentration of the sample a selected frequency. The FPD output signal is then analyzed for the signal component at this frequency which gives the response of the system for particulate sulfur. This system has been described in earlier reports in which several interferences related to SO_2 concentration and relative humidity of the sample were noted. These interferences have been the subject of the most recent work on the system.

A final report on the project will be made after the system has been evaluated in an inter-comparison study with other sulfur and sulfate measurement systems at Washington University, St. Louis, Missouri, in August, 1979. This report will be completed in September 1979.

Activities in the past six months concerned a systematic study of the effect of SO_2 concentration and relative humidity on the system response. The FPD is sensitive to the relative humidity of the sample at the extremes ($\overset{\sim}{<}10\%$ r.h. and $>80\%$ r.h.). The SO_2 interference is quite low, representing less than a few percent equivalent particle sulfate response, and is a difficulty only at very high SO_2 values; however, high values may occur in undiluted or fresh plumes. At very low SO_2 levels the FPD shows nonlinear response and much higher noise. We are now evaluating the feasibility of adding a constant level of gas phase sulfur to bring the total FPD signal up to a better operating range for this detector. The final report will contain a detailed description of this modification and its effect on the system's response.

80-BCL-c-ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

1. Radiocarbon as an Environmental Tracer

Work on the Portland, Oregon aerosol vegetation impact study (in collaboration with Professor J. A. Cooper, Oregon Graduate Center (OGC)) has been completed during the reporting period, as well as a review of the application of carbon isotopes to carbonaceous pollutant source discrimination for the Division of Environmental Chemistry, ACS. A summary was presented in a special symposium (in cooperation with OGC group) at Research Triangle Park on June 20, 1979.

The vegetative burning study represented a major step in the successful application of the mini-radiocarbon (llc) method, for it was the first time size-fractionated particles had been measured using ^{14}C, and it was the first time the technique had been used with known source impacts (field, slash, residential-wood burning). The research served a) to demonstrate the validity of the method in the field, and b) to underline the potentially serious impact of residential wood burning on fine carbonaceous particles in urban locales. Two important future approaches to increase the power of the method were noted in the above studies: the use of chemical (chemical mass balance) and isotopic (^{14}C, ^{13}C) selectivity, and the complementary use of accelerator mass spectrometry (ams).

Although llc and ams are presently comparable with respect to sample size and overall precision, we believe that ams has considerable potential for improvement, provided that sufficient attention is given to ion source chemistry. With this in mind we undertook a series of experiments to couple the technique of separation and implantation of 30 keV Co^+ ions in metal foils by Isotope Separation (IS) with high energy (-20 MeV) acceleration of sputtered ions from the carbon-foil source to count ^{14}C atoms rather than β-particles from their decay. Using CO_2 as the sample gas and high purity copper and aluminum as target foils, we studied molecular ion fragmentation patterns, sputter-cleaning with a 20 keV Ar^+ beam, and implantation-saturation phenomena. With a reasonable understanding of carbon contaminating levels and implantation saturation (∿ 1μg/cm^2), we prepared a series of calibration samples (oxalic acid standard and dilutions) plus one dated archeological wood sample for radiocarbon measurement by ams at the University of Rochester. Samples were delivered on May 15th, 1979, and we are currently awaiting ^{14}C machine-time (mid-July).

Current work includes also preparations for calibration of the new radiocarbon-dating oxalic acid standard and installation of a dedicated data acquisition computer system. In connection with the standard calibration, we are establishing operating characteristics and quality control for the large (∿1.6L), low-level "Oeschger" counter. The sample, which has already been obtained, is derived from a 1978 sugar beet crop and its specific activity is therefore about 30% above the previous standard (due to nuclear testing). We shall count several grams of carbon with the intent of obtaining ∿0.5% accuracy. The Cromenco z-2 computer system has been installed and debugged; and acquisition of test data reflecting actual coincident and anticoincident events has been accomplished. Programs ARDAQ and ARPULS, for acquisition of two dimensional spectra, Energy vs ADP, net counting rates, and test pulses, are currently being checked. Further expansion of our data processing system will include linking the laboratory microcomputer with the NBS 1108 Digital Data Network (NBSNET). This expansion will provide easy access for statistical processing of all counting data and will allow for correlation analysis of counting results with laboratory environmental parameters, e.g. continuously monitored room temperature, humidity and barometric pressure.

80-BCM-a-ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

1. Energy Related Water Pollutant Standard Reference Materials

1.a. Complete Certification of Ocean Sediment SRM

No activity in this project during the last six months.

1.b. Estuarine Sediment, Proposed SRM 1646

No activity in this project during the last six months.

1.c. Anions in Water SRM

No activity in this project during the last six months.

1.d. Trace Elements in Water SRM

Certification analyses for SRM 1643, Trace Elements in Water, are complete. The material will be available for distribution pending, a final compilation and analysis of data.

1.e. The Role of Internal Standardization in Analysis of Aqueous Samples Using the Inductively Coupled Plasma (ICP) Technique

Inductively Coupled Plasma (ICP) Emission Spectrometry

Previous studies with ICP have isolated sources of non-random variability in the measurement technique (1). Experience has shown that proper introduction techniques of aqueous samples can minimize these effects. These include bracketted and averaged standard solution integrations as well as the use of a peristialtic pump with the cross-flow nebulizer.

In minimizing head pressure effects with the peristaltic pump, it is necessary to match the number of rollers, rotation rate, tubing size, and data integration period so that the inherent pulsation of the pump is effectively averaged during one integration period. For example, the following specifications have given satisfactory results:

Number of rollers	10
Rotation rate	22 RPM
Tubing I.D.	0.76 mm
Resulting flow rate	∿1 mL/min.
Integration period	30 *s*

In cases where significant background shifts from samples to standards occur, it is necessary to measure background intensities on either side of the analysis line (2). Present instrumentation does not allow such a measurement without excessively lengthening the total analysis time. Therefore, the first application of the ICP to accurate certification determinations was limited to a few minor constituents in Coal and Coal Fly Ash, Standards Reference Materials (SRM) 1632a and 1633a, respectively. The certificates for these materials have yet to be issued in final form. ICP results are as follows:

SRM	Element	$\bar{x} \pm 2s$
1632a	Ca	2.16 ± 0.08 mg/g
1633a	Sr	818 ± 7 μg/g
1633a	Zn	222 ± 8 μg/g

Contracts have recently been awarded for the new spectrometer and computer system mentioned in the previous report. Installation should be completed by September, 1979.

Eschelle Spectrometer

A continuum-source Eschelle Wavelength Modulation - Atomic absorption Spectrometer (CEWM-AA) is currently being evaluated for the determination of trace metals in a wide variety of samples. The CEWM-AA system offers unique advantages over existing commercial atomic absorption instruments. In CEWM-AAS, superior background correction is provided for <u>all</u> major types of spectral interferences encountered in atomic absorption analyses. Moreover, CEWM-AAS provides accurate background compensation for larger amounts of nonspecific source attenuation which may allow the direct determination of trace metals in highly complex matrices such as lubricating oils, coal, fly ash, and environmental water samples without extensive sample preparation. However, the most attractive feature is the potential capability of CEWM-AAS for fully background-corrected, simultaneous multielement AA analyses using either flame or electrothermal atomization devices.

The CEWM-AA technqiue using electrothermal atomization has been shown to provide accurate and precise results when operated in the single-element mode for a number of trace metals in environmental water samples compare favorably with results obtained by a commercial, line-source AA instrument and other independent analytical techniques. Lubricating oil samples diluted in methyl isobutyl ketone (MIBK) have also been analyzed by CEWM-AAS for silver and tin.

Proposed studies involving CEWM-AAS focus primarily on the optimization of analytical conditions for the determination of eight trace metals (Cd, Cr, Cu, Pb, Mn, Ni, V, and Zn) in coal and ultimately use this technique in the SRM Certification program of these trace metals in other energy related materials. Additional work is required to fully develop CEWM-AAS into a practical, background-corrected, simultaneous multi-element AA technique for the rapid analysis of coal and other energy-related materials.

2. SRMs for Organic Analysis

2.a/b Production of an Aqueous PAH SRM

In previous reports we have described generator columns as an ideal method for preparing saturated (standard) solutions of individual polynuclear aromatic hydrocarbons (PAH). Initial plans were to issue individually certified anthracene, benz(a)-anthracene and benzo(a)pyrene generator columns as a Standard Reference Material (SRM) for PAH in Water by early 1979. We, however, experienced some difficulties in finding a vendor willing to produce this material, due to the potential hazards involved. We have now received a bid from an interested vendor and are in the process of awarding the contract.

Preparation of Aqueous Solutions Containing Several PAHs Using Generator Columns

Although they do not generate saturated solutions, generator columns coated with three or more compounds could be of more practical value. The initial attempt to prepare such a column met with only limited success. A column that was composed of fifty milligrams each of phenanthrene, 1-methylphenanthrene, anthracene, and 2-methylanthracene coated on 20 grams of glass beads, was prepared. The results of this experiment are reported in Table 3. After 6 liters of water had been pumped through this "Generator Column" (G-1), equilibrium had not been achieved.

The same four compounds were used in a second attempt to prepare a generator column that would be capable of generating a stable solution of these four components. The amounts of each compound comprising the one percent coating on the glass beads was made to be proportional to its aqueous solubility.

The results reported in Table 4 demonstrate the feasibility of this approach. After initial conditioning, over six liters of solution were generated with the maximum change being less than 10 percent over that range.

A third generator column (G-3), loaded with three compounds, was prepared by the same technique used to prepare G-2. The column was purged with 5000 mL of water at 25 °C after which a state of equilibrium was reached. Although the concentrations generated by this column were not equal to the equilibrium saturation concentrations for the individual components, they never changed by more than ±5% while more than 6000 mL of water was purged through the column (see Table 5). The concentrations of the individual compounds in the effluent of this column over this interval at 25 °C were:

Anthracene	62.1 ± 1.3 μg/kg
2-Methylanthracene	13.3 ± 0.2
1,2-Benzanthracene	10.8 ± 0.3

Table 3. Effluent Stability of "Generator Column" G-1

Water Purge Volume (mL)	Phenanthrene Conc. (μg/kg)	1-Methyl-phenanthrene Conc. (μg/kg)	Anthracene Conc. (μg/kg)	2-Methyl-Anthracene Conc. (μg/kg)
100	610	167	22.1	14.6
500	541	155	26.0	15.9
860	520	148	26.6	15.1
1330	506	150	29.1	15.7
4500	405	157	34.9	15.5
5350	388	162	35.4	15.8
5550	380	164	36.1	15.9
6400	377	170	35.2	17.7
$\bar{x}$ (1300-6400 mL)	411 ± 53	161 ± 7.6	34.1 ± 2.9	16.1 ± 8.9
Maximum Range between high and low value	29%	13%	19%	12%

Table 4. Effluent Stability of "Generator Column" G-2

Water Purge Volume (mL)	Phenanthrene Conc. (µg/kg)	1-Methyl-phenanthrene Conc. (µg/kg)	Anthracene Conc. (µg/kg)	2-Methyl-anthracene Conc. (µg/kg)
25	913	96.3	12.1	12.2
550	897	73.6	20.1	9.6
2250	890	71.8	18.4	11.1
3700	906	69.9	16.6	10.2
5200	898	70.8	16.4	10.0
6320	888	74.4	16.0	8.94
7100	903	71.0	17.0	10.3
8100	876	78.1	16.5	9.24
$\bar{x}$ (2250-8100 mL)	894 ± 11	72.7 ± 3.1	16.8 ± 0.9	10.0 ± 0.8
Maximum Range between high and low value	1.8%	8.1%	5.8%	19.5%

Table 5. Effluent Stability of "Generator Column" G-3

Water Purge Volume (mL)	Anthracene (µg/Kg)	2-Methyl-anthracene (µg/Kg)	1,2 Benzanthracene (µg/Kg)
200	63.6	13.3	15.8
2000	58.9	11.9	14.0
5000	62.0	13.3	10.9
6000	64.1	12.9	11.0
7200	62.8	13.4	10.7
8100	62.2	13.4	11.0
9300	61.7	13.2	10.7
9990	60.6	13.1	10.4
11500	61.0	13.4	11.1
$\bar{x}$ (5000-11,500 mL)	62.1 ± 1.3	13.3 ± 0.2	10.8 ± 0.3
Minimum Range between high and low value	5.5%	3.0%	6.3%

However, since saturated solutions are not generated by multi-PAH generator columns, the composition of the generated solutions would vary from column to column and would be a function of the volume of water purged through the column. These factors make the production of SRM's via this process unlikely at this time.

2.c. Interlaboratory Comparison Exercise

Samples of an intertidal sediment were received from W. D. MacLeod of the NOAA National Analytical Facility in Seattle, Washington. These samples are part of an interlaboratory comparison exercise. The sediments were received frozen on dry ice and stored at -10 °C until analyzed. The following parameters were to be determined:

1. Chromatographic elution patterns and data
2. Qualitative analysis
3. Quantitative analysis of single species and total hydrocarbon content
4. Percent water in samples
5. Recovery efficiency data

The samples are being analyzed presently, using techniques discussed in previous reports. We are participating in this exercise to both validate our general methodology and to check the effect of refinements to this methodology upon analyses of potential future SRM material.

2.d. Spectroscopic Certification Technique for Analysis of Trace Organics in Water SRM

A new, primary laboratory measurement technique is being developed for the analysis and certification of Standard Reference Materials and the performance of referee-type measurements of trace regulated organics in water. This new method involves laser Raman scattering from pollutants isolated in cryogenic matrices.

The work to date has been focussed on the optimization of matrix preparation and spectroscopic techniques; proving the scientific feasibility of this technique for the analysis of complex mixture of volatile organics (of the type currently regulated by the EPA) at the sub-nanogram level. Although in the developmental stages, this technique should provide a molecular specificity and sensitivity comparable to, or better than, existing techniques currently utilized for water quality assessment. We are investigating the martix isolated laser Raman diagnostic for several reasons: 1) Raman spectroscopy is vibrational spectroscopy and as such provides a characteristic and reproducible "fingerprint" that carries structural information to allow for the unambiguous identification of unknown contaminants; 2) all molecules have characteristic Raman spectra in an experimentally convenient spectral range; 3) the matrix substrate (in this case argon) is free of organic contaminants and has no spectral interferences; it is transparent and allows the vibrational frequencies of the trapped pollutant to be readily compared to the gas phase values of known, pure compounds; 4) at the low temperature used, all rotational motion is frozen out; the spectral linewidths are very sharp, so sharp that the overlapping of bands observed in solution and in the gas phase is not a overlapping of bands observed in solution and in the gas phase is not a problem. The apparatus will be suitable for interfacing directly to a gas chromatograph column for automated sample processing.

Spectra have been routinely obtained from laboratory samples of regulated volatile organics exhibiting spectral features of less than 1 cm^{-1} width. Under these conditions molecular isomers are readily distinguished. With our present, and far from optimum, optics and low-power laser we can readily detect nanogram quantities of a wide variety of volatile species.

Work is just beginning on the analysis of real work samples and on extending this technique to the examination of PAH species.

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80-BCM-b-ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

1 Develop Organic Standard Reference Materials for the Calibration of Energy-Related Water Pollutant Measurement Methods

Current measurement methodology is not adequate for the development of SRM's required to support effective montoring programs for energy-related organic water pollutants. Thus, the activity in this element is closely related to activity in the BCK-b element and efforts over the past six months have focussed on the development optimization of measurement methods capable of measuring trace organics in complex matrices created by new energy technologies so that SRM's can be produced to support the establishment of effective monitoring systems.

Analysis of aqueous effluents from coal conversion processes has been initiated with the receipt of our first effluent samples. Two aqueous effluents from Solvent Refined Coal (SRC) Pilot Plant were analyzed for their phenol and _o_-cresol concentrations. The samples consisted of a BioUnit effluent and a Plant effluent.

As seen in Figure 4, the BioUnit effluent is treated by filtering through sand and charcoal, and then mixing with solidification belt cooling water to generate the Plant effluent.

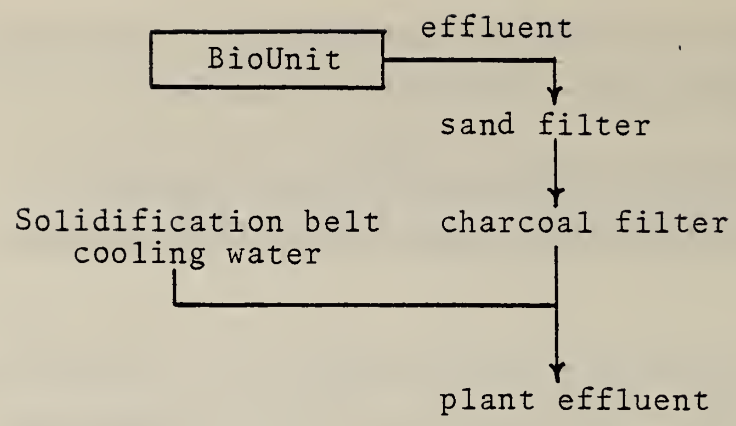

Figure 4

A simple, one-step extraction procedure was used to isolate an acidic fraction from the samples. A 50 mL aliquot of the sample was adjusted to pH 1 with dropwise addition of concentrated H_2SO_4 and then extracted with 25 mL CH_2Cl_2. The organic extract was dried by filtering through a cone of Na_2SO_4, and the volume was reduced to 100 μL by evaporation under a stream of dry N_2. Extraction recoveries for phenol, o-cresol, and p-cresol were determined in an independent experiment. The phenols were added to H_2O at the 1 ppm level and extracted with CH_2Cl_2 as described above. Absolute recoveries were determined based on chromatographic peak heights using an external standard method (see Table below.

Table 6

	Absolute recovery			Recovery relative to p-cresol	
Sample	phenol	o-cresol	p-cresol	phenol	o-cresol
14M-1A	53%	71%	70%	0.75	1.01
14M-1B	51	69	68	0.75	1.01
14M-1C	57	75	72	0.79	1.04
	54±3	72±3	70±2	0.76±0.02	1.02±0.02

An internal standard method was used for quantitative determinations. Preliminary single ion monitoring (SIM) gas chromatographic/mass spectrometric analysis of the BioUnit and Plant effluent extracts revealed the presence of phenol and o-cresol, and a barely detectable amount of p-cresol (see Figure 5). Since the p-cresol was present at a level at least 2 orders of magnitude lower than the phenol and o-cresol, it was chosen as the internal standard.

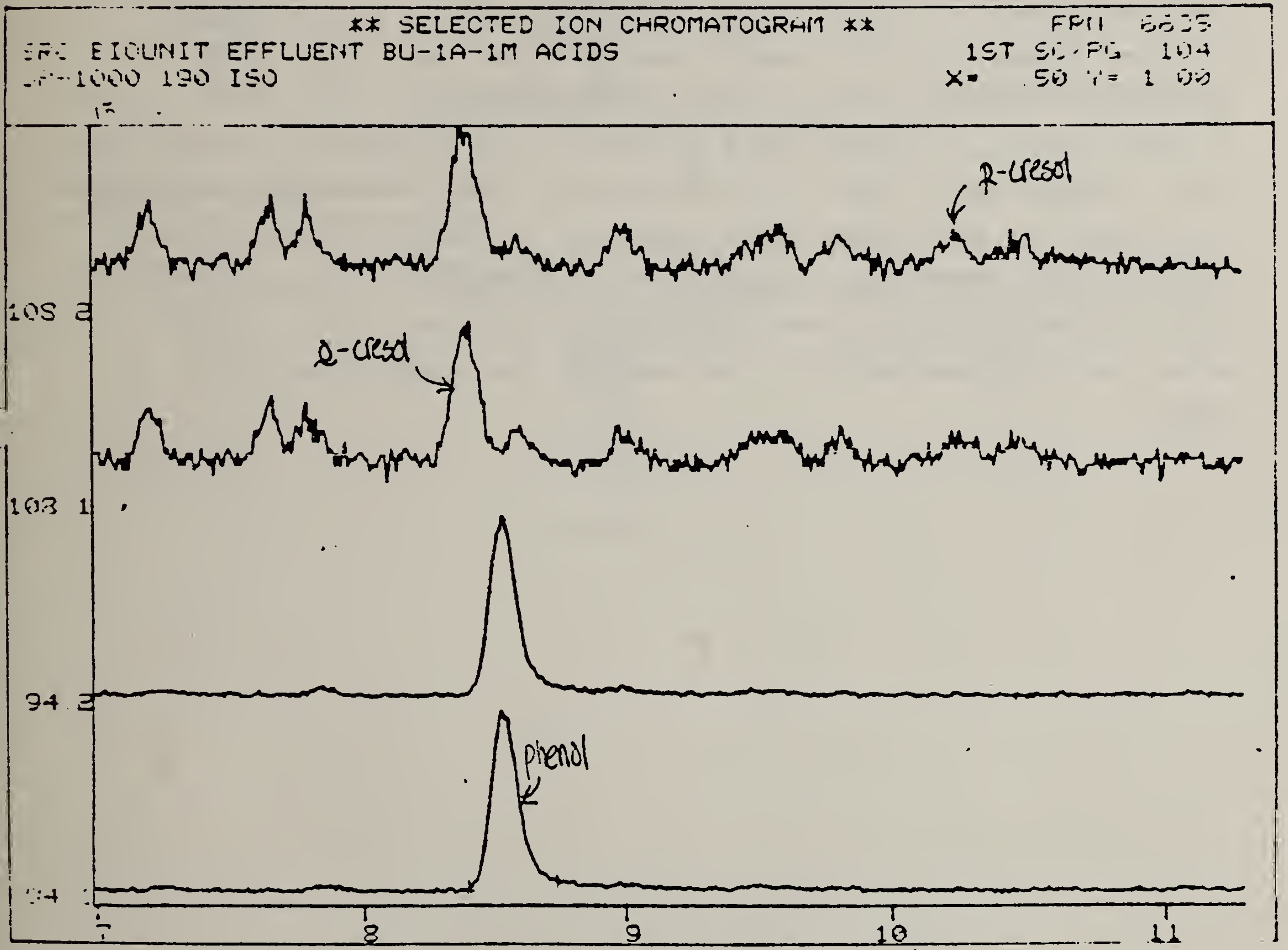

Figure 5. SIM analysis of SRC BioUnit effluent acids.

p-Cresol was added to aliquots of the BioUnit and Plant effluents at the 1 ppm level. The samples were extracted (in duplicate) and analyzed by gas chromatography/mass spectrometry with selected ion monitoring. Gas chromatographic separations were carried out on a 30m x 0.3 mm id SP-1000 wall coated open tubular capillary column operated isothermally at 190 °C. Although the o-cresol and phenol are not completely resolved under these conditions, the use of selected ion monitoring allows determination of each compound free of interferences from the other. The molecular ions for phenol (m/e 94) and o and p-cresol (m/e 108) were monitored over the course of the chromatographic run. Peak areas for the phenol, o-cresol, and p-cresol were determined after each run. Phenol and o-cresol concentrations were determined from the corresponding peak areas, the internal standard concentration, the relative extraction recoveries, and relative response factors for the phenol and o-cresol relative to p-cresol which were determined independently. The results are summarized in Table 7.

Table 7

SRC Plant Effluent H_2O

Sample	Phenol Conc. (ppb)	o-Cresol Conc. (ppb)
PE-15M-A	19.6	1.98
PE-15M-A	18.8	1.98
PE-15M-B	18.4	2.15
PE-15M-B	18.3	2.38
	$\bar{X}$= 18.3 ± 0.59	2.12 ± 0.19

SRC BioUnit Effluent H_2O

Sample	Phenol Conc. (ppb)	o-Cresol Conc. (ppb)
BU-16M-A	37.9	2.94
BU-16M-A	40.9	3.52
BU-16M-B	371.1	3.35
BU-16M-B	36.7	3.23
	$\bar{X}$= 38.2 ± 1.9	3.26 ± 0.24

80-BCN-ENERGY RELATED POLLUTANTS AND EFFECTS MONITORING AND ASSOCIATED METHODS AND TECHNIQUES DEVELOPMENT

1. Radiological Pollutant Quality Assurance

The goal of the program is to provide measurement traceability, through the U. S. Environmental Protection Agency at Las Vegas (EPA-LV), for certain radionuclides not included in other programs. These radionuclides were chosen because they are released into the environment from nuclear power reactors (such as light-water reactors), coal burning plants, or other, related, sources. The program for FY 76-80 is summarized in Table 8.

Table 8

Radiological Pollutant Quality Assurance[a]
Performing Agency: National Bureau of Standards
(Revised Milestones as of June 1979)

Δ - due; ▲ - completed

Task 1. Radiological calibrated radioactive materials	FY 76	FY 77	FY 78	FY 79	FY 80
1.1 Establish lab facility	▲				
1.2 ^{210}Po solution	▲				
1.3 ^{226}Ra soil,		▲			
Mixed gamma solution,		▲			
^{239}Pu solution		▲			
1.4 Mixed gamma soil			▲		
1.5 Natural U solution,			▲		
^{241}Pu soution			▲		
1.6 Fly ash from coal[b]				▲	
1.7 ^{232}Th solution,				▲	
Mixed radionuclide solutions				Δ	
1.8 ^{210}Pb solution					Δ

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[a] Issuances of all Standards are subject to satisfactory performance as defined by NBS Standard Reference Material criteria.

[b] An additional $31k was allocated for (1) traceability testing, which will be a continuing program, and (2) preparation of the fly ash standard.

1.a. Solution of Plutonium-241

We are continuing to measure the half life of plutonium-241 by means of α-γ -coincidence measurements of the ingrowth of americium-241.

1.b. Fly Ash from Coal Combustion

Fly ash from the combustion of eastern United States coal has been assayed for radium-226 and radium-228. The material has been checked for homogeneity, packaged, and sent to EPA-LV. Radium-226 was assayed both by radon counting of radiochemically processed samples and nondestructively by Ge(Li)-detector γ-ray spectrometry. The radium-228 concentration was determined by Ge(Li)-detector γ-ray spectrometry of the actinium-228, bismuth-212, lead-212, and thallium-208 progeny of radium-228.

A second set of γ-ray spectrometric measurements have been made to determine whether the radioactive equilibrium between thorium-232 and radium-228 was disturbed during combustion of the coal. The radium-228 concentration was found not to have changed during the eight-month period between the two sets of γ-ray emission-rate measurements. The report of calibration for this material is being prepared.

1.c. Thorium-232 Solution

Approximately 220 ampoules containing a solution of aged thorium-232 nitrate have been prepared. Six of these ampoules have been assayed by mass spectrometry, and a report of calibration is being prepared to accompany 200 ampoules of solution to EPA-LV.

1.d. Mixed Radionuclide Solutions

The assayed components of a forthcoming mixed radionuclide solution, containing tritium, strontium-90, cesium-134, radium-226, radium-228, and natural uranium, are being assembled. Two solutions with different radioactivity concentrations are to be prepared, and 200 ampoules of each solution are to be provided to EPA-LV.

2 Measurement Traceability Studies with the Quality Assurance Branch of EPA-LV

The NBS conducts tests with the Quality Assurance Branch (QAB) to ascertain whether radioactivity measurements made by the QAB are traceable to NBS. These studies are on radioactive test sources, with known but undisclosed values, that are sent to the QAB by NBS, and on radioactivity standards prepared by the QAB and sent to NBS for confirmatory measurements. The criteria for conducting the studies are given in an appendix to the NBS-EPA interagency agreement of April 1976.

During this six-month reporting period, NBS has provided the QAB with seven test sources, and no results have been reported to NBS. The seven test sources are described in Table 9.

TABLE 9

Test Sources Provided to the Quality Assurance Branch (EPA-LV) by NBS During the First Six Months of 1979.

Parent Radionuclides	Form	Month Sent	Remarks
Hydrogen-3	Solution	February	
Manganese-54	Solution	March	
Strontium-89	Solution	February	Contains strontium-90 and stable calcium as interferences
Strontium-90	Solution	February	Contains barium-133 and stable calcium as interferences
Thorium-232	Solution	March	
Americium-241	Solution	February	
Plutonium-242	Solution	May	