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Isotopic Determination of Uranium in Picomole and Subpicomole Quantities

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A procedure for the separation of U and measurement of U isotopes in meteoritic, lunar, and terrestrial samples is described. Accurate $^{238}U/^{235}U$ ratios and U concentration measurements can be done on a routine basis at the level of $\sim 10^{-13}$ mol of U by isotope dilution using a double tracer composed of ^{233}U and ^{236}U. Precise determination of the number of U atoms in a sample can be done at the level of 10^8–10^9 atoms. The technique involves careful control of the chemical procedures to eliminate laboratory contamination and precise calibration of the mass spectrometer in order to obtain high reproducibility. The $^{238}U/^{235}U$ ratios were measured on a wide variety of samples which include (1) bulk meterorites, (2) lunar samples, (3) coarse-grained Ca–Al–Ti-rich inclusions and (4) fine-grained Al–Mg–Na-rich inclusions from the Allende meteorite, and (5) phosphates from three meteorites. The results show the same isotopic values within limits of errors as that measured on normal terrestrial U to within 4‰. All of the analyzed meteorite samples are very ancient and several of them show large fractionations of U relative to Th and Nd. These data imply that ^{247}Cm was not abundant in the early solar system (^{247}Cm/^{235}U $\ll$ 4 × 10^{-3}) and that the last major "r" process terminated at $\sim 10^8$ years prior to the formation of the solar system.

We report on procedures that permit the accurate isotopic measurement of $^{238}U/^{235}U$ at the level of from 10^{-12} to 10^{-14} mol of natural uranium from both meteoritic and terrestrial samples on a routine basis and without serious laboratory contamination. Accurate concentration measurements can thus be done at levels of 10^{-14}–10^{-16} mol of U. This technique permits us to analyze both the concentration and isotopic composition of U on 10^{-3} g of meteoritic samples which contain on the order of 40 pmol/g of U. Experimental conditions also allow us to analyze both the concentration and isotopic composition of Pb on the same samples as those used for U analyses. This may be applied to dating by the U, Th, and Pb methods (1, 2) and will significantly improve the precision of the U/Pb ratio. The application of this technique can reduce the amount of material required for routine analysis of some actinide elements and with somewhat larger samples could improve the precision of determination of ^{235}U in a variety of applications.

The procedures for high-precision isotopic measurements of U reported here were developed in order to test claims that the U isotopic composition was variable in nature (3) and the

Table I. Uranium Content of Reagents

reagent	^{238}U content, atoms/g
H_2O^a	1.0 × 10^8
HCl (6 M)^{b,c}	1.0 × 10^8
HNO_3 (16 M)^{c,d}	2.5 × 10^8
HF (50%)^{c,d}	1.7 × 10^8
HBr (9 M)^{c,d}	3.1 × 10^8
$HClO_4$ (70%)^e	2.4 × 10^9
total blanks	
microchemistry	5 × 10^9–1.0 × 10^{10} atoms
macrochemistry	~ 2.5 × 10^{10} atoms
filament loading blank	8 × 10^8–2.0 × 10^9 atoms

^{a} Deionized water triple distilled in SiO_2 stills. ^{b} Prepared by bubbling HCl gas in H_2O. ^{c} Twice distilled in Teflon bottles (subboiling distillation) as was described in Mattinson (23). ^{d} "Suprapur" reagents from E. Merck. ^{e} From Frederick Smith Chemical Co.

inference that ^{247}Cm ($\tau_{1/2}$ = 1.56 × 10^7 years) was abundant in the early solar systm (4). The purpose of this report is to document our procedure and to report analyses on some meteoritic materials. The U concentration was determined by isotope dilution using a tracer composed of ^{233}U and ^{236}U. This permits a reliable determination of instrumental discrimination and yields high-precision isotopic abundance of $^{238}U/^{235}U$.

EXPERIMENTAL SECTION

Our approach was to establish adequate procedures which take into account (1) contamination, (2) chemical yield and purity, (3) ionization efficiency, (4) abundance sensitivity, (5) instrumental fractionation, (6) linearity of detector, (7) resolution of shifts in $^{238}U/^{235}U$, and (8) reproducibility. No effort was made to measure the abundance of ^{234}U. All errors listed in this paper are $2\sigma_{mean}$ errors of the values reported. The techniques were then used to show that (9) U concentration measurements could be made on small samples without chemical separation.

(1) **Contamination.** The usual procedure for measuring U is by isotope dilution using ^{235}U as a tracer, which results in the presence of rather large amounts of pure ^{235}U in the laboratory environment. The use of some commercial U_3O_8 which was usually depleted in ^{235}U in some laboratories could also result in the presence of almost pure ^{238}U in the laboratory. The contamination levels necessary to produce a 1% shift in ^{235}U abundance for a sample of 10^{-2} g of meteoritic material are 2 × 10^7 atoms of ^{235}U. The possibility of contamination at this level must be a cause of great concern and as a result (1) we discontinued any handling of separated ^{235}U in the laboratory, (2) all labware which would be in direct contact with the sample during chemical processing was replaced with new materials, and (3) we used a mass spec-

trometer which was previously never used for U measurement and regularly removed and cleaned the ion source.

(2) Chemical Yield and Purity. Samples of meteoritic fragments were prepared by removing all exterior surfaces of the samples as they were received in the laboratory. Large samples (1–1.5 g) were dissolved and processed according to the macrochemistry procedure described below. Small samples of Ca–Al-rich inclusions (10^{-2}–10^{-3} g) were analyzed according to a microchemical procedure.

(a) U Blanks. The labware was vigorously cleaned in acids with the final cleaning done with the high-purity reagents used in the chemical separations. The U contents of reagents (H_2O, HCl, HNO_3, HF, HBr, and $HClO_4$) that are currently in use in this laboratory are less than 10^8 atoms $^{238}U/g$ except that in $HClO_4$ (Table I). The filament loading blank ranges from 8×10^8 to 2×10^9 atoms ^{238}U per experiment. These blanks are small compared with those from the total processing blank. The blank for the total chemical processing and mass spectrometry is 5×10^9 to 1.0×10^{10} atoms of U for the microchemistry procedure and $\sim 2.5 \times 10^{10}$ atoms for the macrochemistry procedure. The $^{238}U/^{235}U$ ratio in the procedural blank was measured to be 140 ± 20.

(b) Macrochemistry. Large samples (1–1.5 g) were digested by soaking in ~ 10 mL of HF (50%) in a covered 50-mL FEP Teflon centrifuge tube and allowed to stand with occasional shaking and swirling of the tube. After ~ 24 h the meteoritic sample usually was disintegrated into a slurry and then transferred into a 30-mL FEP Teflon beaker and evaporated to dryness under a filtered N_2 atmosphere. The sample "cake" was leached with hot 16 M HNO_3 (~ 3 mL) and 70% $HClO_4$ (~ 0.5 mL) and baked with a heat lamp until most excess $HClO_4$ was fumed away. The sample was brought into solution with warm 2 M HCl (~ 20 mL). This solution was centrifuged at $\sim 5 \times 10^3$ rpm for 15 min in the same Teflon tube used previously for digestion. The clear supernate was stored in another 30-mL FEP Teflon beaker. The residue was redigested with a mixture of HF, HNO_3, and $HClO_4$, and brought into solution with 2 M HCl. Usually after two to three cycles of the above digestion steps, essentially no "residue" was observed after centrifugation with a total of ~ 30 mL of 2 M HCl. This solution, derived from the originally insoluble material, was then added to the solution obtained from the previous cycle of digestion. An aliquot (3–10%) was spiked to determine the amount of U (and Th, Pb) and the balance then spiked to give $^{238}U/^{236}U \approx 12$. The spiked solution was evaporated to dryness and redissolved in 2 M HCl.

U was coprecipitated with other group 2 major elements with NH_4OH at pH ~ 7 and the precipitate removed after centrifugation and washed several times with water. This final precipitate was dissolved with 16 M HNO_3 and the solution was adjusted to ~ 7 M HNO_3. We adopted a separation procedure of U by anion exchange in nitrate medium (7–8 M) first reported by Carswell (5). The advantages of this procedure were (1) very few other ions are known to adsorb on the resin under these conditions (6), (2) the conversion of the anion resin to nitrate form is rapid and simple, (3) U can be simply eluted with H_2O or weak acid, and (4) the U salt is a nitrate which has a high solubility in dilute HNO_3.

Anion exchange resin, Dowex AG1×8, 100–200 mesh was rinsed with distilled water in a Teflon bottle. The mixture was allowed to stand for a few minutes and the suspension containing fine particles decanted. The resin was loaded onto a silica glass column (200 mL) and washed with 1 L each of the solutions in the sequence following H_2O–HNO_3 (1 M)–HNO_3 (7 M)–HNO_3 (1 M)–H_2O–HCl (6 M)–H_2O. The clean resin was stored in water until use.

The column used for the separation of U (Th and Pb) is 10 cm long and 0.7 cm i.d. (capacity of 4 mL) made of polyethylene, fitted with a polypropylene plug at the bottom and a 10-mL capacity cup at the top. Clean anion exchange resin was loaded onto the column to a level below the bottom of the cup. The resin was washed with H_2O and 6 M HCl and conditioned with 7 M HNO_3. The solution containing the sample (~ 5 mL) was then loaded onto the column and allowed to drain. The removal of most elements except U (and Th) was accomplished by washing the column with a total of 8 mL of HNO_3 (7 M). If Pb was also being analyzed, then the effluent and the previously drained

sample solution were saved. U (and Th) was removed from the resin column by passing a total of 10 mL of H_2O and 10 mL of 1 M HBr. This U- (and Th-)rich solution was evaporated to dryness and was ready for the next cleanup step with a smaller (0.5 mL) column which will be described in the microchemistry section.

(c) Microchemistry. For smaller samples (<0.1 g) the amount of acids used for digestion was scaled down. Sample digesting was carried out in a 5-mL PFA Teflon beaker (with a snap-on cover). After two cycles of dissolution with HF, HCl, and HNO_3, the samples were brought into clear solution with 7 M HNO_3. The procedure, when applied to Ca–Al-rich inclusions from Allende, left an insoluble residue which consisted almost exclusively of spinel ($MgAl_2O_4$) and contributed from about 10% to 90% of the original sample. The spinel-rich residue was dissolved in a mixture of HF and HNO_3 in a pressurized Teflon bomb (7) at 210 °C for 24 h and was brought to a clear solution in a mixture of HCl and HNO_3. Samples of the more easily soluble silicates and the spinel-rich residues were analyzed sparately in order to determine the U in each type of material. A small aliquot (~ 3%) was spiked to determine the amount of U (Th and Pb) and the balance spiked to optimum isotopic ratios. The spiked solution was evaporated to dryness and redissolved in 7 M HNO_3.

The sample solution in 7 M HNO_3 was loaded directly onto a 0.5-mL anion exchange resin column (Dowex AG1×8, 100–200 mesh) which was previously cleaned and conditioned with 7 M HNO_3. The column is 4 cm long, 0.4 cm i.d. (capacity of 0.5 mL), is made of TFE shrinkable Teflon, and is fitted with a polypropylene plug at the bottom. The resin was washed with a total of 1 mL of 7 M HNO_3 and U was removed with 3 mL of 1 M HBr. The U- (and Th-)rich solution was evaporated to dryness, and the residue was dissolved with a few drops of 6 M HCl. The anion resin column was reloaded with new resin and reconditioned with 6 M HCl and the U (and Th) solution was then loaded on it. Th and other impurities were washed out by passing a total of 1 mL of 6 M HCl, and the final purified U was removed with 3 mL of 1 M HBr. Usually, U separated at this stage was of very high purity and was ready for mass spectrometric measurement.

(d) Chemical Yields. The chemical yields of U for the ion exchange are 95% to 100% and for the total procedure range from 80% to 95%.

(3) Ionization Efficiency. The ionization efficiency is among some of the most important factors in measuring the U isotopic composition by surface ionization mass spectrometry. Following Arden and Gale (8), we used graphite to carbonize a Re filament and to enhance U^+ ion emission. The procedure used by us was to load a suspension of colloidal graphite in water onto a previously outgassed Re filament. This was gently heated to evaporate the H_2O and yielded a thin uniform layer of graphite. The U sample was then loaded on the filament in 0.1 M HNO_3 and dried. Another drop of the graphite suspension was then deposited and dried making a sandwich with the U between the graphite layers. The filament was made out of a strip of zone-refined rhenium ribbon and was outgassed at 2200–2400 °C for 2 h at a pressure of 10^{-8}–10^{-7} torr prior to use. For the best result, we usually coated the Re filament with graphite immediately after outgassing. The ion beam intensity ($^{238}U^+$) for 8.4 pmol of U loaded on the filament was 5×10^{-13} A at the detector for 2–3 h for filament temperatures between 1700 and 1750 °C. The geometry of the Re filament is either (1) a "V-shaped" (9) or (2) a "dimple" (10) one. The latter geometry allows loading of a U sample on a smaller area and seems to give better results for smaller samples (<10^{11} atoms). The ionization efficiency (U^+/U) for 10^8–10^{12} atoms of U ranges from 0.6% to 1.2% for standard solutions. The U ionization efficiency from the standard solutions is in general a factor of 2 better than that obtained from the separated samples. The difference may result from the presence of trace amount of impurities (such as Th) which compete with and suppress the ionization of U^+ ions.

(4) Abundance Sensitivity. The operation and design of the Lunatic mass spectrometer ($r_M = 30$ cm) has been reported previously (11). For measuring U isotopes, we set the source slit at 0.25 mm and the collector slit at 0.64 mm. The abundance sensitivity is between 10^{-5} and 10^{-6} for $\Delta M/M = 1/238$, which is adequate for the measurement of a $^{238}U/^{235}U$ ratio of 137.88 for a normal terrestrial U. During all experiments, we scanned the mass range 230–240 (Figure 1) and did not observe any signal

Table II. Isotopic Composition of U in the ^{233}U-^{236}U Double Spikes[a]

batch	^{233}U/^{236}U [b]	^{234}U/^{236}U	^{235}U/^{236}U	^{238}U/^{236}U
1	1.0066 ± 0.001 [c]	$1.96 \times 10^{-3} \pm 1 \times 10^{-5}$	$5.73 \times 10^{-4} \pm 1 \times 10^{-6}$	$4.38 \times 10^{-4} \pm 4 \times 10^{-6}$
2	1.0144 ± 0.001	$1.95 \times 10^{-3} \pm 1 \times 10^{-5}$	$5.84 \times 10^{-4} \pm 2 \times 10^{-6}$	$5.32 \times 10^{-4} \pm 4 \times 10^{-6}$

[a] Two batches of ^{233}U-^{236}U double spikes were prepared from pure ^{233}U and ^{236}U. Batch 1 was used for the analyses on bulk meteorites (1), and batch 2 for this work and previous work (2) on Allende inclusions and phosphates. [b] Normalized to NBS U-500, ^{238}U/^{235}U = 1.0003 ± 0.001. [c] Errors = $2\sigma_m$.
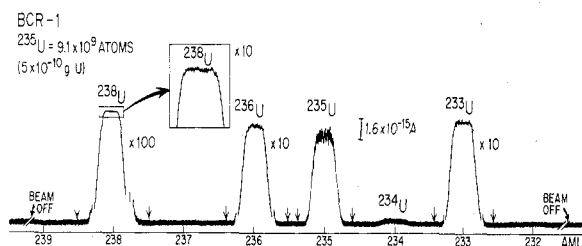

Figure 1. U mass spectrum of terrestrial U (BCR-1). Arrows show where the zeroes were measured. Note the shift in scale.

besides U (and ^{232}Th for some samples). With the ^{238}U$^+$ ion beam at 5×10^{-13} A the signal at M = 235.5 is essentially the same with either beam-on or beam-off (HV-on or -off) corresponding to less than 3×10^{-17} A of primary beam, indicating no detectable contribution of either low-level peak tails from neighboring isotope scattered beams or impurities (i.e., hydrocarbon). The amplifier is quite stable with a drift of less than 10^{-17} A h^{-1}.

(5) Instrumental Fractionation. A ^{233}U-^{236}U double spike prepared from high-purity ^{233}U and ^{236}U was used to monitor mass-dependent isotope fractionation (12, 13). The isotopic composition of the double spike is given in Table II. The absolute ratio of ^{233}U/^{236}U and the concentration in the mixed spike were determined by using a solution of mixed spike and the NBS U-500 standard (99.4% U_3O_8, ^{238}U/^{235}U = 1.0003 ± 0.001) (14) to correct for fractionation. The limiting uncertainty in the ^{233}U/^{236}U ratio in the spike is the error in the NBS U-500 standard, as all ratios used for calibration were near unity. In the analyses, we measured the ion beams (I_M) at mass 233 and 236 in conjunction with 235 and 238 in order to determine the instrumental mass fractionation. At each mass the zeroes and peaks were measured with an integration time of 1 s and a settling time of 3 s prior to signal integration. The mass jumping sequences were cycled in the order ^{238}U-^{236}U-^{233}U-^{238}U and ^{236}U-^{235}U-^{233}U-^{233}U-^{236}U and data taken in sets of 10 ratios. In general, the sample was spiked such that the resulting ^{238}U/^{236}U and ^{236}U/^{235}U ratios were about 12 in order to optimize the dynamic range and precision (1). For larger samples three sets of 10 ratios (^{238}U:^{236}U:^{233}U) were first measurd and then the filament current raised such that I_{236} was similar to that of I_{238} in the preceding sets, and three sets of ^{236}U:^{235}U:^{233}U were measured. The ratios (relative to ^{236}U) in a set were averaged and corrected for discrimination (<2‰ amu^{-1}) and contributions of ^{238}U and ^{235}U from the double spike which were less than 4 × 10^{-2}‰ and 7‰, respectively. The ^{238}U/^{235}U ratio was calculated from the normalized ^{238}U/^{236}U and ^{235}U/^{236}U ratios in the different sets and the error given as the errors of the ^{238}U/^{235}U in $2\sigma_m$. The second ^{235}U measurement in the ^{236}U-^{235}U-^{235}U-^{233}U-^{236}U mass jumping sequence serves to monitor any change in the intensity of I_{235} which might be caused by the decay constant of the detector system. For all measurements on the Lunatic I mass spectrometer the ^{235}U/^{236}U ratios between the first and second sets agree within error limits. For smaller amounts of U (<10^{11} atoms) the mass jumping sequences were cycled in the order ^{238}U-^{236}U-^{235}U-^{235}U-^{233}U-^{238}U and data taken in sets of 20 ratios at different temperature ranges until total exhaustion of the sample.

(6) Linearity of Detector. To test linearity of the detector system the ^{238}U/^{235}U ratio was determined on double-spiked samples as a function of ion beam intensity. The detector system used for U isotopic measurement on the Lunatic I mass spectrometer consists of a 17-stage Cu-Be electron multiplier (gain = 4 × 10^3 at 2300 V) in the current mode and vibrating reed electrometer (Cary 401) with a 10^9 Ω resistor. On an identical detector system on the Lunatic III mass spectrometer we observed previously a decrease in the measured ^{238}U/^{235}U ratios with in-

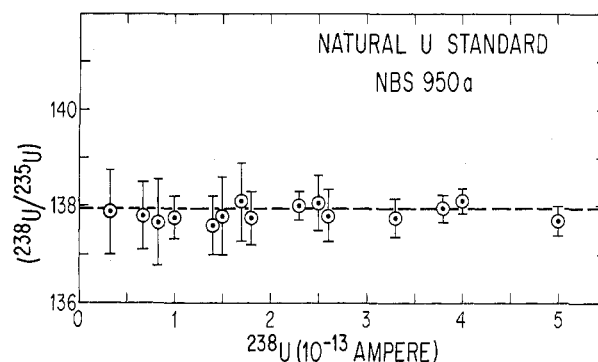**Figure 2.** ^{238}U/^{235}U in natural U standard (NBS 950a) corrected for discrimination using a double spike. Data are shown as a function of ion current. This provides a linearity test of the electron multiplier (current integration mode) on the Lunatic I mass spectrometer.
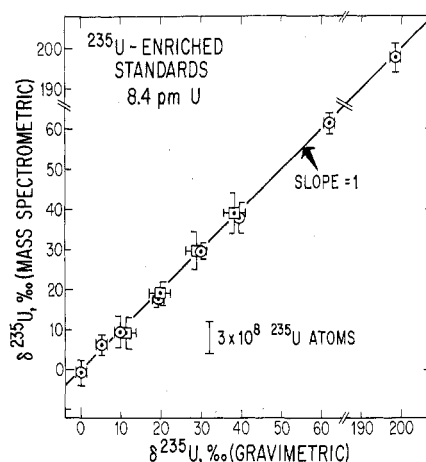

Figure 3. Comparison between gravimetrically determined δ^{235}U and that obtained mass spectrometrically for experiments on enriched U samples (8.4 pmol ^{238}U and ~0.06 pmol ^{235}U). Squares represent data from the first batch of ^{235}U-enriched standards; circles represent the second batch. Note broken scale.

creasing signal and a significant change in both gain and peak shape during a period of 1 year (1). On the contrary, the detector system on the Lunatic I mass spectrometer gave consistent gain and good peak shape over the same period of time. The result of a routine linearity test is shown in Figure 2, indicating no detectable deviation of the ^{238}U/^{235}U ratios within the range of sample current. The linearity and gain of the detector system were tested prior to every sample measurement with a standard U sample containing the double spike.

(7) Resolution of Shift in ^{238}U/^{235}U. To establish the reliability with which shifts in isotopic abundance can be determined, we (a) prepared standards with small enrichments in ^{235}U by mixing different amounts of ^{235}U spike into a standard solution of NBS 950a and ^{236}U-^{233}U tracer and (b) mixed the ^{235}U-enriched standards with aliquots of solutions of a meteorite sample.

(a) ^{235}U-Enriched Standard. The isotopic abundance of U in the ^{235}U-enriched standards (δ^{235}U = 40‰) was measured by loading different amounts of U for each set of experiments. A complete set of comparisons was made for samples of enriched standards ranging from 8.4 to 84 pmol. The results on 8.4 pmol of four enriched standards were published previously (1). Since then, a second batch of seven ^{235}U-enriched standards (δ^{235}U =
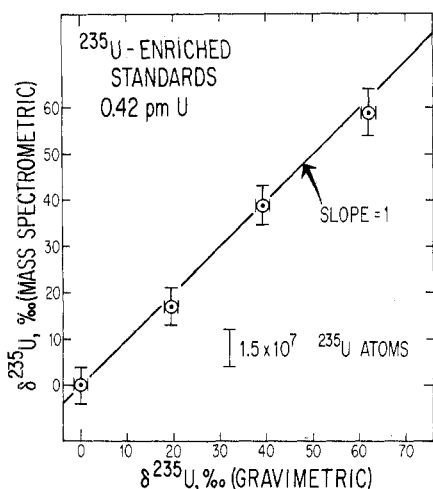
Figure 4. Same as Figure 3, on 0.42 pmol ^{238}U sample.

Figure 5. Comparison between gravimetrically determined δ^{235}U and that obtained mass spectrometrically for aliquots of Egg-1 to which ^{235}U-enriched solutions were added prior to chemical separation.

5–200‰ was prepared and measured. Two sets of enriched standards were used with 8.4 and 0.42 pmol of U per analysis, respectively. The measured ratios after correction for discrimination and contributions of ^{238}U and ^{235}U from the double spike are compared with gravimetrically determined ^{238}U/^{235}U ratios in Figures 3 and 4. The first set (8.4 pmol, Figure 3) of data which includes the results from the first batch of enriched standard indicates that (1) at least 4‰ U isotopic effects can be resolved, and (2) all mass spectrometric measurements for the enriched standards agree with the values calculated from gravimetry. The second set (Figure 4) of data is for the 0.42 pmol ^{235}U-enriched solutions. The results also plot on a 45° line and clearly demonstrate the ability to resolve U isotopic effects above 6‰. This corresponds to the addition of 1.5 × 10^7 ^{235}U atoms to the sample. Using larger samples with a Faraday collector, we believe that it is possible to clearly resolve isotopic shifts of 1‰.

(b) ^{235}U-Enriched Meteorite Sample. In addition to the experiments on the ^{235}U-enriched standards, we added a known amount of ^{235}U to aliquots of a solution from Allende inclusion Egg-1 and then passed these solutions through the chemical separation procedure and analyzed them. The purpose of the experiment was to prove that no isotopic effect was subdued by terrestrial contamination during chemical processing. After dissolution, the solution of acid-soluble phases of Egg-1 was aliquoted into four fractions. A ^{233}U–^{236}U tracer was added to the first fraction (A) to determine the isotopic composition and concentration of the solution. Both ^{233}U–^{236}U and solutions of a ^{235}U-enriched standard were added to the fractions B, C, and D. Fractions C and D were further aliquoted into two fractions which consisted of a large aliquot (90%) and a small aliquot (10%). The different solutions consisting of meteoritic U, ^{233}U–^{236}U tracer and a ^{235}U-enriched standard were than passed through the chemistry and were analyzed. By use of the concentration determined on aliquot A and the concentration and isotopic composition of the enriched standard, the ^{238}U/^{235}U was calculated from the gravimetric data. The measured ratios after correction are compared with gravimetrically determined ^{238}U/^{235}U ratios in Figure 5. These results indicate that (1) all mass spectrometric measurements for the enriched samples agree with the values calculated from gravimetry, (2) a 27‰ and a 90.8‰ shift in U isotopic ratio were readily detected for samples as small as 0.7 and 0.9 pmol, respectively, and (3) no exchange or dilution with normal U took place in the chemistry to subdue any U isotopic effect at the level of 6 × 10^7 ^{235}U atoms.

(8) Reproducibility. We consider one of the most important criteria for a reliable experimental datum to be that of reproducibility. In the previous sections we have shown that the function of the instruments is reliable and predictable and that the isotopic measurements on both normal and enriched U standards are reproducible (both with and without chemical separation). In addition, we have made substantial efforts to repeat all of the measurements to establish reproducibility. Most of the samples we measured were analyzed with at least one duplicate analysis, and all of the data were found to be in good
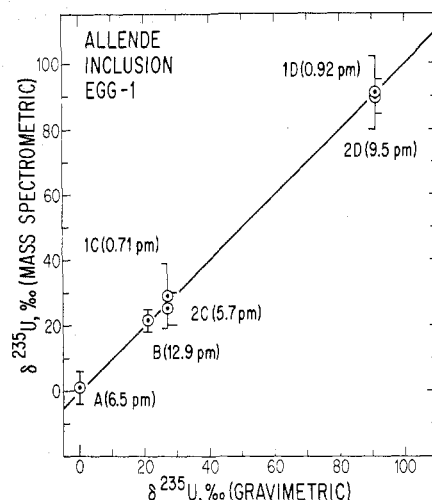
agreement. Some examples are shown in Table III and other results may be found in Chen and Wasserburg (1, 2). We hope that workers who make claims of isotopic anomalies would carry out adequate tests of experimental reproducibility before announcing their results.

(9) U Microanalysis without Chemical Separation. The U mass spectrometric technique described in the previous section demonstrates that precise determination of the number of U atoms in a sample can be done at the level of 10^8–10^9 atoms. In particular, the high ionization efficiency and high running temperature for U isotopic measurements should permit the analysis of rock samples without chemical separation as was demonstrated in the Rb–Sr analyses of lunar samples by Papanastassiou and Wasserburg (15). We tested the technique (modified direct loading technique) with a terrestrial basalt (BCR-1), which contains ~1.7 ppm U and ~6 ppm Th. The sample (2.6 mg) was dissolved to form a clear solution, and aliquots of the solution which contained ~10 μg of dissolved rock (~0.07 pmol ^{238}U, 0.26 pmol ^{232}Th) were spiked with ~4.3 pmol of ^{233}U–^{236}U and ~1.9 pmol of ^{230}Th and were evaporated to dryness. The sample mixture was dissolved and loaded onto a Re filament with graphite (see previous section) and measured on the Lunatic I mass spectrometer. At filament temperature of ~1700 °C, we did not find any other signal besides U and Th isotopes between mass 180 and 240. At the lower mass region, the elements which give signals above 3 × 10^{-16} A are identified as Al, Y, Ca, Ti, Ba, and rare earth elements. The uncertainties on the ^{238}U/^{236}U ratios (~0.02) are 6‰ ($2\sigma_m$) while uncertainties on the ^{233}U/^{236}U ratios are 1‰. The ^{238}U/^{236}U ratios decreased by about 3% when the filament temperature was raised to ~1800 °C. The change in ^{238}U/^{236}U ratios probably indicates depletion of small amounts of ^{238}U in the graphite and Re filament during a run. The ^{230}Th/^{232}Th ratios (~7) were measured with the same filament after the exhaustion of U ions and have uncertainties of 2‰ ($2\sigma_m$). These preliminary experiments showed that it was possible to measure the U and Th in samples with concentrations at the level of 2 ppm on ~10 μg of a dissolved rock without chemical separation and achieve an analysis of the U and Th contents with less than 6‰ error.

To eliminate the uncertainties from loading blanks (Table I), we added natural U (NBS 960) to the sample solution to increase the ^{238}U concentration (to about 21 ppm). Spikes of ^{233}U–^{236}U and ^{230}Th were also added to permit determination of the U and Th concentrations by isotope dilution. A part of this spiked solution was processed through the usual anion exchange resin to separate U and Th. The U and Th isotopic compositions of this processed solution were measured on two aliquots (A-1 and A-2), which contained 0.84 and 4.2 pmol of ^{238}U and 0.26 and 1.3 pmol of ^{232}Th, respectively. The resulting U and Th concentrations are shown in Table IV. In addition, two aliquots (B-1 and B-2) of the original spiked solution (which had not gone through chemical separation) were loaded directly on prepared filaments with graphite. These samples corresponded to 10 and

Table III. U Isotopic Composition

sample[a]	^{238}U pmol[b]	ppb	^{238}U/^{235}U[c]	δ^{235}U,[d] ‰
Allende Coarse-Grained Inclusions (Type B)				
N47 NBS950a	5		138.0 ± 0.3	−0.9 ± 2.1
1. Egg-2A	13.8	60	137.7 ± 0.6	+1.3 ± 4.3
N48 NBS950a	5		137.8 ± 0.7	+0.6 ± 5.1
2. Egg-2B	19.0	61	137.9 ± 0.4	−0.2 ± 3.0
N49 NBS950a	5		137.9 ± 0.4	−0.2 ± 3.0
N50 NBS950a	3		137.9 ± 0.4	−0.2 ± 3.0
3. Egg-2R	0.7	4	137.9 ± 2.8	−0.2 ± 20
N51 NBS950a	2		137.7 ± 0.5	+1.3 ± 3.6
4. Egg-2C	0.35	59	138.0 ± 0.9	−0.9 ± 6.5
N54 NBS950a	5		137.4 ± 0.4	+3.5 ± 3.0
5. Egg-2D	5.0	71	138.1 ± 0.5	−1.6 ± 3.6
6. Egg-3A[e]	9.3		138.1 ± 0.6	−1.6 ± 4.3
7. Egg-3B[e]	34.2	240	137.6 ± 0.4	+2.0 ± 2.9
N45 NBS950a	5		138.1 ± 0.4	−1.6 ± 3.0
8. Egg-3R	0.04	2	136.0 ± 3.4	+14 ± 24
N52 NBS950a	5		138.0 ± 0.3	−0.9 ± 2.2
9. Egg-3D	11.3	136	138.1 ± 0.7	−1.6 ± 5.0
N53 NBS950a	5		137.8 ± 0.3	+0.6 ± 2.2
10. Egg-6B	4.0	64	137.9 ± 0.7	−0.2 ± 5.0
Allende Fine-Grained Inclusions				
N46 NBS950a	5		138.1 ± 0.7	−1.6 ± 5.0
11. Pink Angel-A	1.3	14	137.0 ± 1.5	+6.4 ± 11
12. Pink Angel-AR	0.06	0.6	139.8 ± 5.2	−14 ± 37
N58 NBS950a	5		138.3 ± 0.4	−3.0 ± 3.0
13. Pink Angel-B	1.8	12	138.0 ± 1.1	−0.9 ± 8.0
14. Pink Angel-BR	0.2	1	136.5 ± 1.4	+10 ± 10
Nadiabondi Phosphates				
N57 NBS950a	0.5		137.9 ± 0.6	−0.2 ± 4.4
15. WH-1	0.29	51	137.9 ± 1.0	−0.2 ± 7.0
N56 NBS950a	5		138.1 ± 0.5	−1.6 ± 3.6
16. WH-2	4.6	19	137.5 ± 0.5	+2.8 ± 3.6

[a] Numbered samples are meteoritic samples; others are the U standard which were run on the same date and just prior to the sample listed. Letters (A to D) after sample numbers indicate duplicate analyses of different fragments of the samples. Letter (R) represents residue of each individual samples except that Egg-2R is the sum of residues from Egg-2A and Egg-2B and Egg-3R is the sum of residues from Egg-3A and Egg-3B. [b] Amount of U analyzed. [c] Errors are $2\sigma_{mean}$. All data corrected for mass fractionation and a small contribution of ^{238}U and ^{235}U from the ^{233}U-^{236}U double spike. [d] δ^{235}U = [(^{235}U/^{238}U)$_{measd}$ × 137.88 − 1] × 10^3. [e] From Chen and Wasserburg (2).

Table IV. U and Th Concentrations in BCR-1 with Normal U Added

sample[c]	concns,[a] ppm ^{238}U[b]	^{232}Th
Aliquot A, with Chemical Separation (1300 μg of Rock)		
A-1	20.67 ± 0.016	6.037 ± 0.020
A-2	20.68 ± 0.013	6.020 ± 0.014
Aliquot B, without Chemical Separation (Modified Direct Loading Technique)		
B-1(10 μg of rock)	20.56 ± 0.021	6.080 ± 0.020
B-2(50 μg of rock)	20.57 ± 0.019	6.036 ± 0.015

[a] Error limits are from uncertainties ($2\sigma_m$) in the ^{238}U/^{236}U and ^{230}Th/^{232}Th ratios. [b] Corrected for 1.8 × 10^9 atoms ^{238}U loading blank. [c] The ^{238}U/^{235}U ratios measured on a 10-μg unspiked aliquot are 138 ± 4.

50 μg of the dissolved rock. The isotopic composition of these spiked and directly loaded samples was measured, and the concentrations were determined. The U results on aliquots from the same solution show excellent agreement. The small difference (~6‰) between results from aliquot A (with chemical separation) and aliquot B (without chemical separation) may be from U blanks (loading and chemistry).

In addition, an aliquot of the originally unspiked solution which had not gone through chemical separation was analyzed for U isotopes with the modified direct loading technique. This sample corresponded to 10 μg of the dissolved rock and contained 0.5 fmol

of ^{235}U. The ^{238}U/^{235}U ratios measured in two data cycles (10 ratios per cycle) were 137.8 ± 7.6 (2σ) and 137.6 ± 4.8 (2σ), respectively, and were the same as normal U. Since no double spike was added, these ratios were not corrected for discrimination, but the correction should be small (<2‰ amu^{-1}). It follows that precise and reliable U and Th concentrations and U isotopic composition can be determined on small samples (~10 μg) without chemical separation down to concentrations of a few parts per million.

RESULTS

The samples studied were a variety of Ca–Al–Ti-rich inclusions (type B) from the Allende meteorite, many of which are known to contain ^{26}Mg* (excess ^{26}Mg) from ^{26}Al decay. Some analyzed samples were fine-grained inclusions from Allende rich in Mg, Al, Na, and halogens. All these materials have been known to contain isotopically exotic materials. In addition, phosphates from the Nadiabondi meteorite were analyzed, as it is known to contain the fission products of ^{244}Pu and with a high Pu/U ratio (16–18). Some new U isotopic results are given in Table III and Figure 6 as ^{238}U/^{235}U and as fractional deviations in parts per thousand (δ^{235}U). The amount of meteoritic U measured per analysis ranges from 0.04 to 34.2 pmol. The results on two fragments of a coarse-grained type B inclusion, Egg-2A and -2B, are indistinguishable from terrestrial (Table III). To obtain sufficient material, we combined the residues from Egg-2A and -2B and designated it Egg-2R. This residue (Egg-2R) has a very low U concentration and yields the same isotopic abundance as

Table V. Th/U, Nd/U, and Pu/U in Phosphates

samples	Th/U	Nd/U	Pu/U[a]	ref
St. Séverin	6-12	300-380	0.033	this work and (2, 24-26)
Angra dos Reis[b]	17-21	~220	~0.009	(2, 17, 27-29)
Nadiabondi	9	2.1 × 10³	0.12-0.13	this work and (16-18)
solar system	~3.8	50-70	0.015[c]	(2, 17, 26)

[a] Values at 4.57 AE ago. [b] A magmatic differentiate. A somewhat different value of Pu/Nd = 1.5 × 10⁻⁴ is given by Lugmair and Marti (29). The Pu/U ratio for bulk meteorite was 0.006-0.008 (17, 30). [c] Value for bulk St. Séverin (26).
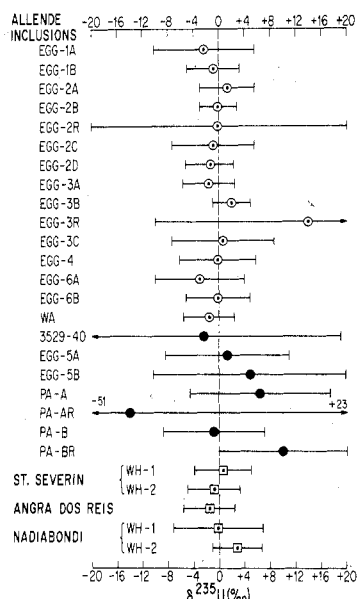
Figure 6. Bar-graph showing the values of $\delta^{235}U$ (‰) in the Allende inclusions and meteoritic phosphates from St. Séverin, Angra dos Reis, and Nadiabondi. The central dashed line represents the terrestrial value of $(^{238}U/^{235}U)\oplus$ = 137.88.

normal U (but with larger errors). Analyses on two more fragments (C and D) of Egg-2 agree with the previous two and have normal U isotopic ratios. The residues from Egg-3A and -3B from our previous work (2) were combined and called Egg-3R and analyzed. The U concentration in the residue, Egg-3R, is again much lower than the easily soluble portion. Measurement on 2.4 × 10¹⁰ U atoms from this residue (Egg-3R) is within error (±24‰) the same as normal U. Results on two more coarse-grained inclusions, Egg-3D and Egg-6B, are similar to that of other fragments of the same inclusions (2) and have normal U isotopic ratios.

Two fragments (A and B) from a fine-grained inclusion, Pink Angel, and their residues (AR and BR) were analyzed (Table III). The easily soluble portions and the residues of the Pink Angel have the same isotopic composition (with larger errors). Both fractions have lower U concentrations than for the type B inclusions. The concentrations in the residues are also much lower than the easily soluble portions. The results indicate that (1) all residues have U isotopic composition the same as that of normal U to within errors, and (2) the residues only contain from 0.8% (Egg-3R) to 6.5% (Egg-2R) of the U from each of the whole inclusions. From these results, we conclude that the U concentration in the residue is so low that it would have to have at least 100‰ isotopic shifts to cause a 10‰ shift in the bulk inclusion. These shifts were obviously not observed.

Phosphates were separated from the Nadiabondi meteorite using heavy liquids followed by a magnetic separation. The yield of phosphate (WH-1, ~100% whitlockite) was ~2 mg from 29 g of meteorite. In addition, a separate (300 mg) of phosphate-rich mixture which contains ~7% whitlockite, ~92% of a mixture of pyroxene, plagioclase, and olivine, and ~1% of a mixture of oxides, sulfide, and metal was obtained.

From this phosphate-rich mixture, 81 mg was analyzed for U isotopes and other elements (WH-2, Table 3). The $^{238}U/^{235}U$ ratios measured on these two phosphate separates (WH-1 and WH-2) are within 3‰ of the normal U value (Table III). The Th/U, Nd/U, and Pu/U ratios in phosphates from Nadiabondi, Angra dos Reis, and St. Séverin are given in Table V. These ratios in phosphates are higher than that in bulk meteorites (or the average solar system values).

In a recent study, Shimamura and Lugmair (19) have also reported the $^{238}U/^{235}U$ ratios in some bulk meteorites, a phosphate and Allende inclusions. For most samples, they found the $^{238}U/^{235}U$ ratios are the same as in normal terrestrial U, but on one chip of a bulk meteorite (Khohar) they reported a small anomaly ($\delta^{235}U \sim -5.5$‰). However, they obtained normal U isotopic values in three other measurements on two different chips of this same meteorite. These authors could not find any plausible explanation why this anomalous result could be an artifact and indicated that they would further pursue this problem. The following discussion will be based on the self-consistent and reproducible data taken in this laboratory.

DISCUSSION

Our new data and previous results on the Allende inclusions, Nadiabondi phosphates, and phosphates from two other meteorites are summarized in a bar graph in Figure 6. The bars represent error limits ($2\sigma_{mean}$) of each experiment. In general, the Allende coarse-grained inclusions have higher U concentrations and more material is available for analyses. These data have uncertainties ($2\sigma_{mean}$) ranging from 3 to 8‰. On the other hand, the Allende fine-grained inclusions and residues from both coarse- and fine-grained inclusions have low U concentrations and less material is available for analyses. Their uncertainties range from 8 to 37‰. Uncertainties for the results from relativley pure phosphates range from 4 to 7‰. Our new results and those reported earlier (1, 2, 20) give strict upper limits on any variation in $^{238}U/^{235}U$ in a wide variety of samples. These samples include (1) bulk meteorites, (2) lunar samples, (3) coarse-grained Ca–Al-rich inclusions from the Allende meteorite, (4) fine-grained Al–Mg–Na-rich inclusions from Allende, and (5) phosphates from three meteorites containing abundant ^{244}Pu decay products. Our previous U isotopic results on ten bulk meteorites and acid leaches on two of them are summarized in Figure 7. The results show that the $^{238}U/^{235}U$ ratios for all bulk meteorites studied are equal, within error limits, to that of normal terrestrial U.

A summary of all the results on meteoritic U isotopic measurements made in this laboratory using the procedures described above is shown in a histogram (Figure 8). The amount of meteoritic U analyzed for each measurement ranges from 0.6 to 34 pmol and about 50% of the samples in Figure 8 are less than 10 pmol. Data from a few residues which have small amounts of U (0.04-0.7 pmol) and have larger errors are not included in this diagram (see Table III). For comparison, the results on terrestrial U (BCR-1 and NBS950a) are also shown in Figure 8. For these terrestrial samples, the amount of U measured ranges from 2.4 to 84 pmol and about 50% are less than 10 pmol. Both the meteoritic and terrestrial U show
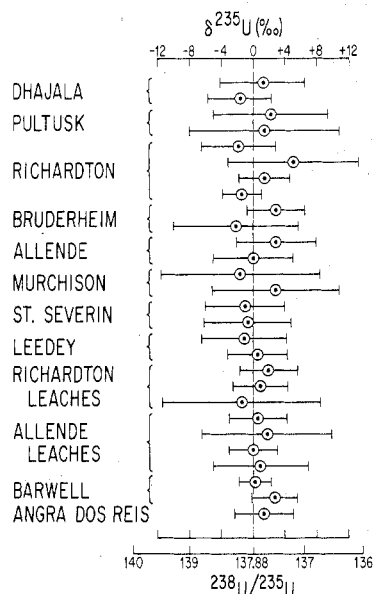
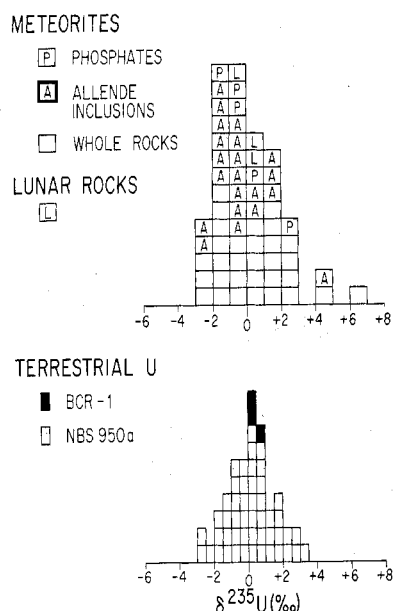**Figure 7.** Bar-graph showing the range of $\delta^{235}U$ (‰) on bulk meteorites and leaches.

Figure 8. Histograms showing the measured $\delta^{235}U$ on meteoritic and terrestrial U. The data of both classes of samples fit a Gaussian distribution with means close to $\delta^{235}U = 0$.

a Gaussian distribution with means close to $\delta\ ^{235}U = 0$, and small dispersion. The average of all meteoritic U isotopic measurements is $^{238}U/^{235}U = 137.83 \pm 0.55$ (2 σ_{GM}) or $\delta^{235}U = +0.4 \pm 4.0$‰, which is indistinguishable from the average for the U standards: 137.85 ± 0.4 ($2\sigma_{GM}$) or $\delta^{235}U = +0.2 \pm 2.8$‰.

The meteorite samples which were analyzed are known to have formed in the early solar system. Several of the samples have U/Th or U/Nd ratios greatly shifted from the average solar values, implying that Cm/U should be substantially shifted if Cm was present. Many of the Ca–Al-rich inclusions which we studied were known to have excess ^{26}Mg in phases with high Al/Mg, and some have isotopic anomalies in other elements (see summary in ref 2). Our results on ten different meteorites and on nine Ca–Al-rich inclusions show no anomaly from either the easily soluble phases or the residual oxides. We also did not find any anomaly in the ^{207}Pb/^{206}Pb ratios on these analyzed samples (2). The present results thus show that the variations in the $^{238}U/^{235}U$ ratios in extraterrestrial

materials as reported by other groups (3, 4) are in error and that there is no observational basis for believing that ^{247}Cm was abundant in the early solar system. We conclude that any variations in ^{235}U abundance in these materials must be less than ~4‰.

If ^{247}Cm were present in sufficient abundance and were fractionated relative to U in some samples under the conditions in the early solar system, it could result in shifts in $^{238}U/^{235}U$ due to the decay of ^{247}Cm (21). We reported previously that the Th/U ratios in some Ca–Al-rich inclusions are highly fractionated (factors of 2–25) but that the $^{238}U/^{235}U$ ratios are normal (2). The Pu/U and Th/U ratios on phosphates from the St. Séverin chondrite, the Nadiabondi chondrite, and the Angra dos Reis achondrite are also highly fractionated (Table V), but the $^{238}U/^{235}U$ ratios were found to be the same as in normal U.

In conclusion, in a wide spectrum of samples which either show isotopic anomalies in other elements or have highly fractionated actinide abundances, we did not observe any variations in the $^{238}U/^{235}U$ ratios to within analytical errors. Nor were any anomalies in the ^{207}Pb/^{206}Pb ratios observed. From the uncertainties of our data, we obtain an upper limit of $^{247}Cm/^{235}U \ll 4 \times 10^{-3}$ at the time of meteorite formation or differentiation, assuming a fractionation of a factor of at least 2 for Cm/U between, say, whitlockite and bulk meteorite. This shows that there was no gross overproduction of the actinides relative to average solar abundance in the more recent nucleosynthesis which made ^{26}Al and ^{107}Pd. These results imply that the last major "r" process terminated at ~10^8 years prior to the formation of the solar system and, from the known $^{244}Pu/^{232}Th$ abundances, that the "r" process events between 4×10^8 and 1×10^8 years prior to solar system formation at 4.57 AE (1AE $= 10^9$ years) ago were 10^2 times larger than the late stage miniburp which produced ^{26}Al, ^{107}Pd, some ^{129}I, ^{41}Ca(?), and possibly the general isotopic heterogeneities (22).

The improved analytical techniques described here have direct application to the precise measurement of U isotopic composition and concentration for a wide variety of materials and also for the reliable determination of U–Pb ages for small samples.

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Vacuum Sublimation and Solvent Extraction of Polycyclic Aromatic Compounds Adsorbed on Carbonaceous Materials

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Glass capillary gas chromatography and flame ionization detector have been used to compare extraction by vacuum sublimation and Soxhlet extraction for the yield of polycyclic compounds originating from carbon black and soot from an aluminum industry. Factors affecting the yield are extraction time, sample amount, and type of solvent. The carbon black sample showed the strongest affinity for the adsorbed compounds and the strength increases with the size (aromaticity) of the compound. The main aromatic extractables were identified by mass spectrometry: PAH, polycyclic aromatic hydrocarbons (mol wt range 176–300), sulfur analogues (mol wt range 208–306), and oxygen derivatives (mol wt range 204–272). Of four investigated solvents (acetone, dichloromethane (DCM), methanol, and cyclohexane) DCM showed the best yield. Vacuum sublimation was equally efficient as DCM, but evaporative losses could be seen for three- and four-ring PAH as well as degradation of labile compounds such as cyclopenteno[cd]pyrene and oxy-PAH containing more than one oxygen atom.

Polycyclic aromatic hydrocarbons (PAH) and derivatives thereof are widespread atmospheric pollutants, mainly originating from the combustion of fossil products (*1*), and the carcinogenic/mutagenic properties of these compounds (*2*) have called for analytical procedures on a routine basis. Evaluation of different methods has been carried out (*3*), but the analytical techniques for determination of PAH have recently undergone significant improvements, and it is now possible to make a more complete separation of complex mixtures (*4*).

However, PAH are often associated with highly sorbtive matrices, which is why a reliable extraction step prior to the analysis is necessary (*5*). A commonly used technique is Soxhlet extraction using different solvents for different periods of time. A number of publications have also pointed out the

advantage of vacuum sublimation as a fast and convenient method for extraction, though few laboratories seem to use the technique. Sublimation has been used to fractionate mixtures of PAH (*6, 7*), and recovery studies from both synthetic and real samples have been made (*8*).

The use of vacuum sublimation for the extraction of PAH from filter media or particulate matter has been described by other authors (*9–12*) but only little information covering the wide boiling point range of PAH or optimization of temperature or time required has been published. A recent paper demonstrated the easy handling which can be achieved with sublimation and thin-layer chromatography (*13*). This paper presents an evaluation of vacuum sublimation as an extraction method compared to solvent extraction for particulate samples, and the need for determination of extraction yield for different matrices is also demonstrated.

EXPERIMENTAL SECTION

The PAH samples in this investigation were particulates from an aluminum reduction plant (soot trapped on an electrical precipitator) and carbon black derived from natural gas and aimed for the printing industry. These carriers contain several PAH and derivatives, Figures 1 and 2, within a wide boiling range.

The vacuum sublimation apparatus is a simple all-glass device, Figure 3, on which trapping is achieved by means of a water-cooled finger (5–10 °C) with a surface of 1600 mm^2. The vacuum chamber is inserted in the oven which is kept at 300 °C, and the pressure is reduced by a vacuum pump to 0.1 torr in about 60 s. After sublimation, the sublimate is collected as a pale yellowish/brownish slick which covers 30–40% of the bulb. The sample is transferred to a 3-mL glass tube by gentle washing with 1 mL of cyclohexane/acetone 2/1. Internal standards are added (β,β'-dinaphthyl and *p*-quarterphenyl) and the sample is analyzed without further cleanup.

Solvent extractions were performed in ordinary Soxhlet extractors (volumes of 50 and 100 mL), and the sample was stored in cellulose thimbles (Munktell no. 401) which prior to analysis were cleaned by extraction for 24 h in the same solvent used for extraction. All extractors were monitored for siphoning rate for each solvent and the temperature setting so arranged as to give