Accuracy in Trace Analysis

Trace Radiocarbon Analysis of Environmental Samples

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1. Radiocarbon in the Environment

In the atmosphere, radioactive ^{14}C is produced at a roughly constant rate and decays with a half-life of 5730 y. Human activity perturbs the natural, steady-state level of ^{14}C. Combustion of fossil fuels and emission of pollutants derived from fossil feedstocks dilute ^{14}C with "dead" ^{12}C (the "Suess effect"), and nuclear weapons tests produce excess ^{14}C (the "bomb effect"). Therefore, sources are often revealed by measurement of ^{14}C in species of environmental concern, such as "greenhouse" gases (CO_2, CO, CH_4), atmospheric particles, and toxic or carcinogenic organic compounds.

Atmospheric weapons testing peaked in the early 1960s, and, in 1963, the atmospheric radiocarbon level was about twice the natural level [1]. Since then, the ^{14}C concentration has been declining, largely because of equilibration of atmospheric CO_2 with carbonate in the world's oceans. The changing distribution of "bomb" carbon in the ocean has been measured to investigate ocean circulation patterns [2,3,4]. As nuclear power plants become more widely used, they, too, may become important sources of atmospheric ^{14}C. Radiocarbon has already been exploited as an inherent tracer to investigate the dispersion of plumes from nuclear power plants [5,6,7].

2. Accelerator Mass Spectrometry

For many species of interest, the small amount of sample available requires the use of accelerator mass spectrometry (AMS) for radiocarbon analysis. A gram of modern carbon undergoes 13.56 radioactive disintegrations ($^{14}C \rightarrow ^{12}C$) per minute; this corresponds to a ^{14}C concentration of 5.9×10^{10} atoms of $^{14}C/gC$. Because AMS detects atoms rather than radioactive decays, it is far more sensitive than conventional counting methods.

In AMS, a Cs^- ion sputter source is used to produce negative ions from a sample target. The major interference with ^{14}C is ^{14}N, which does not form stable negative ions and hence is largely eliminated. In many AMS systems, the mass-14 beam is selected by a magnetic deflector and directed into a tandem accelerator. The ions are accelerated at ~ 3 MeV and gas-stripped. At this energy, the most probable charge state for C is $+3$. Interfering molecular ions, e.g., ^{13}CH and $^{12}CH_2$, are unstable in the $+3$ state and disintegrate completely. The ion beam is then accelerated back to ground potential, the mass-14, $+3$ beam is selected, and final measurement of ^{14}C occurs in E-dE/dx detectors of the type used in nuclear physics. Magnetic switching between ^{14}C and ^{13}C or ^{12}C permits the measurement of ^{14}C relative to a stable isotope.

At present, the accuracy of AMS is limited by contamination during sample preparation, sensitivity (response/^{14}C) by ionization efficiency and half-life, and precision by counting statistics and "machine reproducibility" (currently $\sim 0.5\%$ for mg-size samples). A sample-preparation technique developed at NBS [8] involves a closed-tube combustion of samples to CO_2 followed by a closed-system reduction to CO over hot Zn and reduction of CO to C on Fe wool. The procedure, giving an overall blank (chemistry and accelerator) of 1.9 ± 0.4 μg contemporary carbon, has been used to measure samples containing < 100 μg of carbon (RSE = 10%) [9].

Development of gaseous ion sources that can accept CO_2 directly [10,11] will reduce sample handling and hence contamination. When such sources become available, combined techniques such as GC-AMS will be possible, since samples eluting from a column could be combusted to CO_2 and introduced directly into the AMS ion source [12].

3. Radiocarbon in Atmospheric Particles

Carbonaceous particles in the atmosphere are of interest not only because of their effects on visibility, climate, and health but also because they may carry toxic or carcinogenic organic pollutants. Radiocarbon analysis allows modern particles arising from biological processes or from human activities

such as wood-burning to be distinguished from those arising from fossil sources such as motor traffic and combustion of coal and oil.

Because of the large sample requirements of conventional decay counting, early work [13,14] involved collection of whole-particle samples over long periods (days). Such whole-particle samples are often biased by the presence of relatively large debris such as pollen, insect parts, and road dust, but the fine (<2.5 μm diameter) particles are of more environmental concern. Fine carbonaceous particles have a disproportionate effect on visibility and climate [15] and are in the "respirable" size range, i.e., they are retained in the lungs. Measurement of size-fractionated aerosol in Los Angeles [16,17,18] showed that the fine particles had a higher percentage of fossil, anthropogenic carbon than did larger particles.

Our involvement with EPA's Integrated Air Cancer Project (IACP) [19] allowed us to investigate the sources of different chemical fractions in fine particles. Samples were collected during winter, 1984–1985, in two cities (Raleigh, NC, and Albuquerque, NM) where the dominant carbon sources were expected to be residential wood combustion (contemporary) and motor vehicle emissions (fossil). We used oxidation with nitric acid [20] to isolate the elemental carbon fraction from selected fine-particle samples and analyzed both elemental and total carbon for ^{14}C. The results summarized in table 1 show that: (1) as expected, the

fossil (motor vehicle) contribution was highest for the high-traffic intersection in the daytime and was quite low for the residential sites at night; and (2) the elemental carbon fraction had a higher fossil contribution than the corresponding total carbon in all cases. This result suggests that elemental carbon may be more useful than total or organic carbon for tracing mobile sources [21].

Finally, in a second Albuquerque study conducted in December 1985, we isolated the polycyclic aromatic hydrocarbon (PAH) fraction from fine-particle samples. The behavior of two PAH, dehydroabietic acid (DHA) and benzo(ghi)perylene (BGP), is shown in figure 1. DHA has been detected in wood smoke [22], and BGP has been suggested as a tracer for motor vehicle emissions [23]. The utility of these and other PAH as source tracers will be tested by comparing PAH-based source-strength estimates with ^{14}C results for the PAH fraction.

Acknowledgments

Table 1. Radiocarbon results for IACP samples

Site	% Contemporary	
	Total C	Elemental C
Raleigh, residential site		
night	95±14[a] (3)[b]	60±11 (2)
Albuquerque, residential site		
night	78±6 (8)	61±10 (8)
day	66±2 (2)	40±18 (3)
Albuquerque, traffic intersection		
day	35±15 (3)	19±1 (2)

Contemporary carbon values have been adjusted for the ^{14}C content of the atmosphere.

[a] Errors shown are standard deviations.

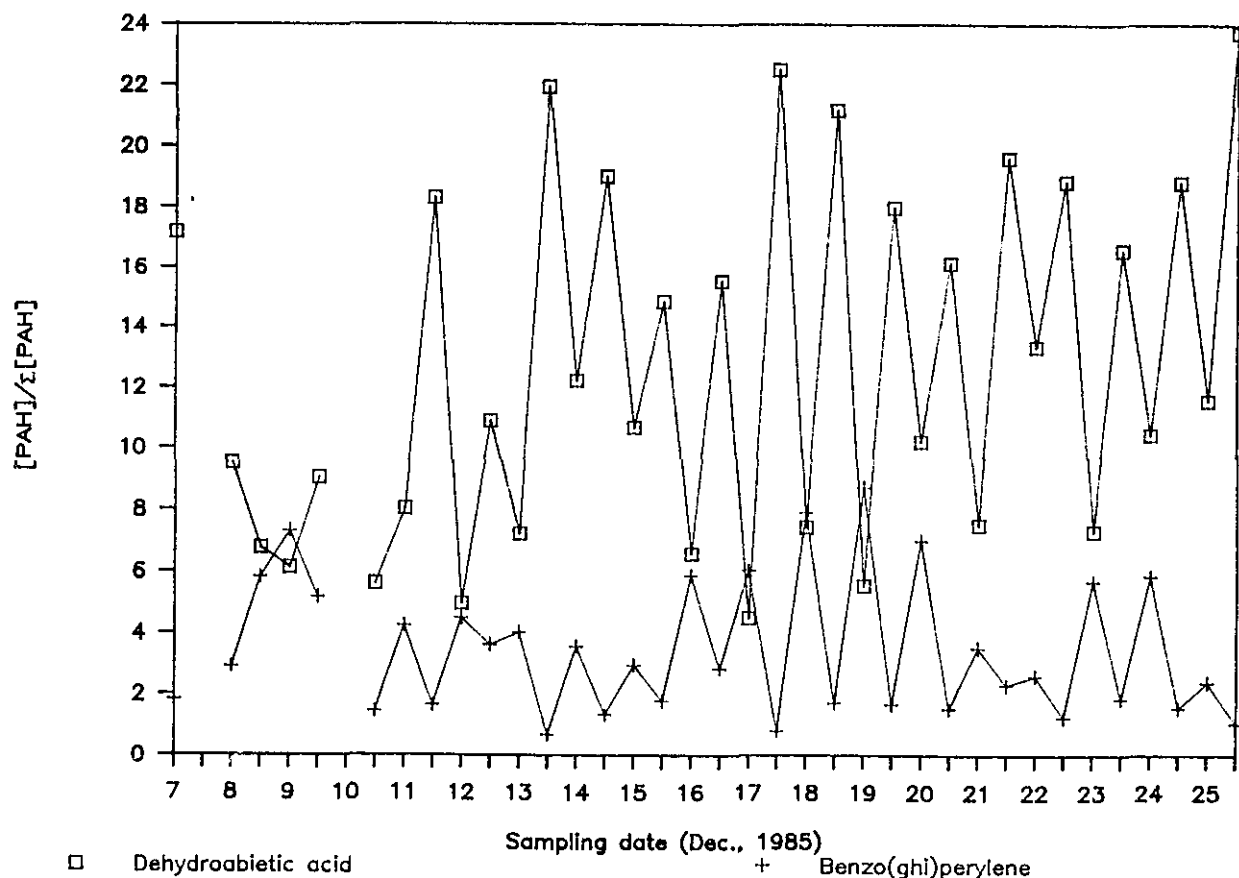[b] The number of samples (N) for each entry is given in parentheses.

Figure 1. Variation of DHA and BGP with collection date and time in samples from a residential site in Albuquerque, NM. For each sample, PAH concentrations are expressed relative to the total mass of all PAH measured in that sample. Integral "date" values represent daytime samples; half-integral values indicate nighttime samples.

References

[1] Levin, I., Münnich, K. O., and Weiss, W., Radiocarbon (U.S.) 22, 379 (1980).

[2] Broecker, W. S., Peng, T.-H., Ostlund, G., and Stuiver, M., Geophys. Res. (U.S.) 90, 6953 (1985).

[3] Peng, T.-H., Radiocarbon (U.S.) 28, 363 (1986).

[4] Schlitzer, R., Radiocarbon (U.S.) 28, 391 (1986).

[5] Walker, A. J., Otlet, R. L., and Longley, H., Radiocarbon (U.S.) 28, 681 (1986).

[6] McCartney, M., Baxter, M. S., McKay, K., and Scott, E. M., Radiocarbon (U.S.) 28, 634 (1986).

[7] Otlet, R. L., Walker, A. J., and Longley, H., Radiocarbon (U.S.) 25, 593 (1983).

[8] Verkouteren, R. M., Klouda, G. A., Currie, L. A., Donahue, D. J., Jull, A. J. T., and Linick, T. W., Phys. Res. B (Netherlands), in press (1987).

[9] Klouda, G. A., and Currie, L. A., Verkouteren, R. M., Einfeld, W., and Zak, B. D., J. Amer. Nuclear Soc. (U.S.), in press (1987).

[10] Middleton, R, Phys. Res. B (Netherlands) 5, 193 (1984).

[11] Bronk, C. R., and Hedges, R. E. M., Phys. Res. B (Netherlands), in press (1987).

[12] Gillespie, R., Radiocarbon (U.S.) 28, 1065 (1986).

[13] Clayton, G. D., Arnold, J. R., and Patty, F. A., Science (U.S.) 122, 751 (1955).

[14] Lodge, J. P., Jr., Bien, G. S., and Suess, H. E., Internatl. J. Air Pollution 2, 309 (1960).

[15] Wolff, G. T., Countess, R. J., Groblicki, P. J., Ferman, M. A., Cadle, S. H., and Muhlbaier, J. L., Atmos. Environ. (U. K.) 15, 2485 (1981).

[16] Currie, L. A., Klouda, G. A., Continetti, R. E., Kaplan, I. R., Wong, W. W., Dzubay, T. G., and Stevens, R. K., Radiocarbon (U.S.) 25, 603 (1983).

[17] Klouda, G. A., Currie, L. A., Donahue, D. J., Jull, A. J. T., and Zabel, T. H., Phys. Res. B (Netherlands) 5, 265 (1984).

[18] Berger, R., McJunkin, D., and Johnson, R., Radiocarbon (U.S.) 28, 661 (1986).

[19] Lewtas, J., and Cupitt, L., Overview of the Integrated Air Cancer Project, Proc. 1987 EPA/APCA Symposium on Measurement of Toxic and Related Air Pollutants, APCA, Pittsburgh (1987), p. 555.

[20] Sheffield, A. E., Klouda, G. A., and Currie, L. A. in preparation (1987).

[21] Klouda, G. A., Currie, L. A., Sheffield, A. E., Wise, S. A., Benner, B. A., Stevens, R. K., and Merrill, R. G., The Source Apportionment of Carbonaceous Combustion Products by Micro-Radiocarbon Measurements for the Integrated Air Cancer Project (IACP), Proc. 1987 EPA/APCA Symposium on Measurement of Toxic and Related Air Pollutants, APCA, Pittsburgh (1987), p. 573.

[22] Standley, L. J., and Simonheit, B. R. T., Environ. Sci. Technol. (U.S.) 21, 163 (1987).

[23] Sawicki, E., Analysis for Airborne Particulate Hydrocarbons: Their Relative Proportions as Affected by Different Types of Pollution, National Cancer Institute Monograph No. 9 (1962).

The Use of Cryogenic Size Reduction to Improve Purgeable Priority Pollutant Analyses in Soil Samples

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Air Products and Chemicals has been investigating the use of cryogenics to improve the recoveries of priority pollutants from solid matrices. A significant number of benefits have been realized from cryogenic size reduction of materials prior to analysis. The precision and accuracy of trace organic analyses in solid matrices are improved by cryogenic techniques. Even the most difficult samples, from rocks to rubber, can be easily ground cryogenically. Cryogenic size reduction increases sample homogeneity, reduces analyte loss due to the heat of grinding, and improves extraction efficiency by increasing the surface area of the sample.

The Environmental Protection Agency (EPA) has proposed the Toxicity Characteristic Leaching Procedure (TCLP) to identify wastes which pose a hazard due to their potential to leach toxic species. Because the determination of volatile species was important, a Zero Headspace Extractor (ZHE) was designed to prevent volatile loss during leaching. A shortcoming of the proposed volatiles analysis is that a trade-off had been made between size reduction and volatile loss. The EPA recommends that only solids that are >9.5 mm or have a surface area of <3.1 cm²/g be reduced.

Clays were used as the synthetic soil matrix from which volatiles would be recovered. Clays have a number of unique properties which make them ideal candidates for adsorbing and retaining volatile organics. A hardened clay matrix was produced by combining one part kaolin clay, one part sepolite clay, one part cement, and two parts water. Twenty-one volatile organic priority pollutants were spiked into the clay matrix via the aqueous portion of the formulation. The spiking was performed at two concentrations, 20 mg/kg and 2.0 mg/kg in the solid matrix.

The spiked clay samples were reduced to 9.5 mm under ambient conditions, reduced to <200 mesh at ambient temperature, or reduced to <200 mesh at cryogenic temperature (-196 °C). After size reduction, the sample was extracted for 18 h in the ZHE according to TCLP protocol. The leachate was then analyzed by purge and trap GC/MS according to the EPA method #624.

At the 20 mg/kg spike concentration, recoveries ranged from 1.2% to 20%. Recoveries never approached 100% because a significant portion of volatiles was lost to the atmosphere during mixing and hardening of the clay-cement matrix. On a relative basis, cryogenic size reduction improved recoveries three fold over ambient and minimum size reduction techniques.

At the 2 mg/kg spike concentration, the effects of cryogenic size reduction were also quantified. Recoveries were improved an average of five times over ambient and minimum size reduction. Analysis precision, as measured by the percent relative standard deviation between three extractions, was also improved. The precisions of analyses were 5.9% for cryogenic size reduction (200 mesh @ -195 °C), 13% for minimum size reduction (9.5 mm @ 20 °C) and 25% for ambient size reduction (200 mesh @ 20 °C). These results indicated that when cryogenic size reduction was not possible, minimum size reduction was preferred.

Cryogenic grinding was clearly the best size reduction technique for the preparation of samples for volatile analysis. Advantages were increased analyte recovery, better sample homogeneity, and improved extraction efficiency.