this improvement and improvements in the detector and the laser stability, the device should be able to quantitatively measure NO concentrations to better than 0.1 ppm. With an intracavity configuration the sensitivity of the device can be extended to the range of parts per billion.

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Lead Isotopes in North American Coals

Abstract. *Lead isotopes in North American coals are equally or much more radiogenic than those in the present continental crust (a mean composition for the continental crust is used). It is practicable to distinguish coal and gasoline lead pollutants by examining their isotopic compositions.*

Atmospheric lead pollution is well documented (*1*), and the ambient lead concentrations are far above those naturally occurring (*2*). In 1968 an estimated 184,316 tons of lead aerosols were emitted in the United States. Of this, some 181,000 tons of lead were attributed to the combustion of leaded gasoline, and 920 tons were attributed to coal burning, the second largest emission source. In regions where coal burning prevails, studies have indicated lead concentrations as high as 150 ppm in fly ash and 358 ppm in soot near coal-burning electric power plants (*3*).

Each natural lead deposit has a characteristic isotopic composition, and this unique property has been used to trace lead pollutants in the environment (*4*). The isotopic compositions of coal leads may make it possible to differentiate the sources of emission.

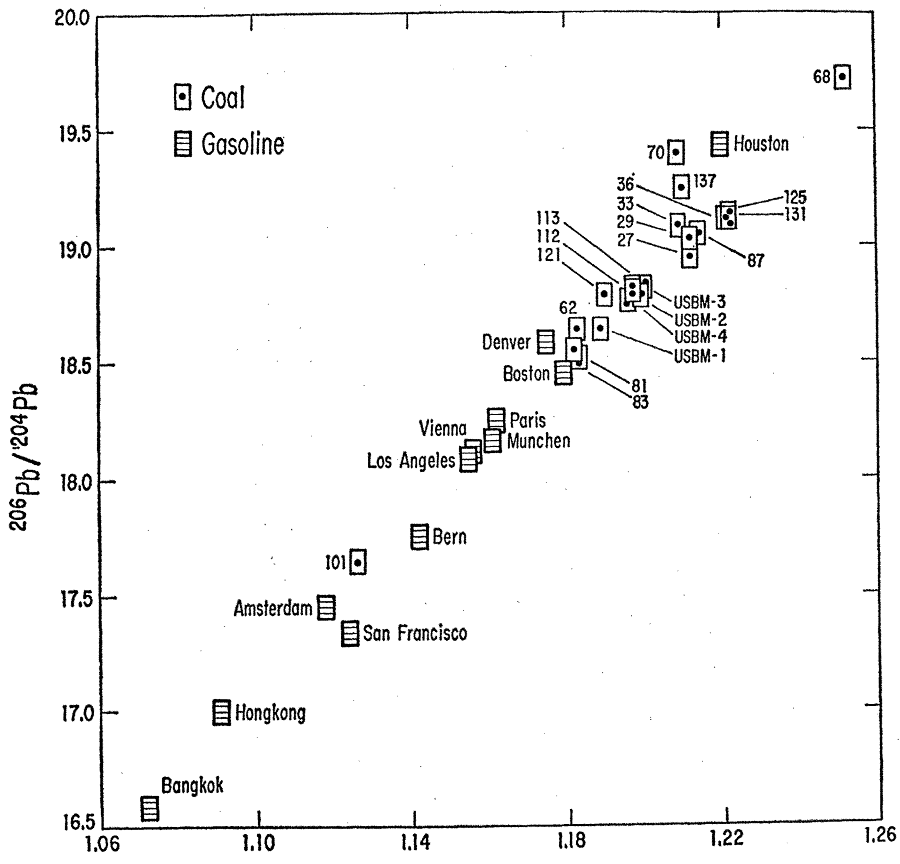

Fig. 1. Comparison of isotope ratios of coal and gasoline leads. The rectangular dimensions indicate the measurement errors.

Coal samples were obtained from various North American coal provinces. Coals of the Eastern and the Interior provinces were deposited during the Pennsylvanian age, those of the Rocky Mountain province during the Mesozoic age, and those of the Great Plains and the Pacific Coast provinces during the Tertiary age.

The washed coal samples were pulverized to 100 to 200 mesh size, weighed, and ashed at 400°C to constant weight. The lead was extracted by treating the ash with concentrated nitric and perchloric acids, isolated by standard ion-exchange technique, purified by several dithizone extractions, and then converted to the sulfide form for isotopic analysis. Mass spectrometry was performed with a solid-source instrument (radius 30 cm) with an electron multiplier. Corrections proportional to the square root of the mass ratio are incorporated in the data to compensate for velocity discriminations in the electron multiplier. The following limits (90 percent confidence interval) were assigned to the lead isotope ratios: ± 0.3 percent of the ^{206}Pb/^{204}Pb ratio, ± 0.1 percent of the ^{206}Pb/^{207}Pb ratio, and ± 0.2 percent of the ^{206}Pb/^{208}Pb ratio.

We have determined the lead contents of 143 coal samples, which contain an average of 11 ppm of lead (96 ppm on an ashed basis). The details of the lead concentration data will be discussed elsewhere. Some 21 samples were selected and analyzed for their lead isotopic composition (Table 1). The isotope ratios show that coal leads are equally or much more radiogenic than the average lead in the present continental crust. Lead isotope ratios in the continental crust, based on analysis of marine sediments, are 18.45 for ^{206}Pb/^{204}Pb and 1.182 for ^{206}Pb/^{207}Pb (*5*). The isotopic composition of the lead in the coal samples showed no correlation with the age of plant accumulation or coalification. However, the radiogeneity of the lead in the coal is inversely proportional to the lead concentration. This is evidenced by coal samples 62, 81, 83 and USBM-1 (Table 1), which contain high lead concentrations (between 33 and 170 ppm) and the least radiogenic lead. This can be explained by the gradual accumulation of common lead by the coal from its matrix after deposition of the original plant material, the common lead diluting the radiogenic lead components produced by the decay of radioactive uranium and thorium (*6*). Coal samples 68 and 70 are from the Mississippi Valley region and contain the so-called J-type lead, which has high percentages of radiogenic components. The rest of the coal samples have lead concentrations less than 14 ppm, and their isotopic compositions fall between the two extremes.

Coal sample 101 is an exception, having an isotopic composition less radiogenic than that of the earth's crustal lead. The specimen seems to be not contaminated, and the probable explanation is that this coal may have incorporated some lead of an old model age through geologic time.

Table 1. Isotopic lead compositions of North American coal samples. The coal classifications are abbreviated as follows: b, bituminous; hvAb, high volatile A bituminous; sub, subbituminous; hvBb, high volatile B bituminous; subA, subbituminous A; mvb, medium volatile bituminous; and lig, lignite.

Sample	Pb (ppm)	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{206}\text{Pb}/^{207}\text{Pb}$	$^{206}\text{Pb}/^{208}\text{Pb}$
Eastern province (Pennsylvania region), Pennsylvanian (Westphalian) age				
USBM-1. Huber Wanamie and Sugar Notch seams, Huber Colliery, Ashley, Pa.	33.8	18.64	1.189	0.4824
USBM-2. Jeddo seam, Highland No. 5 Plant, Jeddo, Pa.	10.7	18.82	1.197	0.4850
USBM-3. Trevorton and Alaska seams, Trevorton Breaker, Trevorton, Pa.	10.0	18.82	1.200	0.4849
USBM-4. Knickerbocker, Oak Hill, Pine Forest, Beechwood, and Buck Run seams, St. Nicholas Breaker, St. Nicholas, Pa.	13.5	18.79	1.199	0.4848
Eastern province (Appalachia region), Pennsylvanian (Westphalian) age				
27. Lower Cedar Grove seam (b), Adanac mine, Mingo County, W.Va.	6.3	18.96	1.212	0.4892
29. Eagle and Campbell Creek seams (b), Kopperston mine, Wyoming County, W.Va.	5.3	19.04	1.212	0.4930
33. Powellton seam (b), Reedy mine, Wyoming County, W.Va.	4.0	19.08	1.209	0.4891
36. Splash Dam seam (b), Five Oaks mine, Buchanan County, Va.	4.0	19.11	1.222	0.4953
Interior province (Eastern region), Pennsylvanian (Westphalian) age				
62. Springfield No. 5 seam (b), Buckheart No. 17 mine, Fulton County, Ill.	37.4	18.64	1.183	0.4808
68. No. 9 seam (b), East Diamond mine, Hopkins County, Ky.	7.7	19.72	1.252	0.5091
70. No. 9 seam (b), Pleasant View mine, Hopkins County, Ky.	13.5	19.40	1.209	0.4915
Interior province (Western region), Pennsylvanian (Westphalian) age				
81. Paw Paw seam (hvAb), White Oak mine, Craig County, Okla.	120.7	18.55	1.182	0.4795
83. Knifton seam (hvAb), Clemens No. 25 mine, Crawford County, Kan.	170.2	18.52	1.183	0.4813
87. Upper and lower Hartshorne seams (hvAb) Evans mine, Haskell County, Okla.	3.8	19.05	1.214	0.4908
Northern Great Plains province (Bighorn Basin region), Paleocene age				
101. No. 3 seam (sub), Foster Creek mine, Carbon County, Mont.	7.2	17.64	1.126	0.4700
Rocky Mountain province (Uinta region), Cretaceous (Campanian) age				
112. Lower Sunnyside seam (hvBb), Sunnyside No. 3 mine, Carbon County, Utah	4.7	18.77	1.196	0.4835
113. Lower Sunnyside seam (hvBb), Columbia mine, Carbon County, Utah	5.3	18.80	1.197	0.4846
Rocky Mountain province (San Juan River region), Cretaceous (Campanian) age				
121. Seams 6, 7, and 8 (sub), Navajo mine, San Juan County, N.M.	9.9	18.78	1.190	0.4807
Cretaceous (Coniacian) age				
125. Fuchsia seam (subA), McKinley mine, McKinley County, N.M.	5.7	19.12	1.222	0.4908
Rocky Mountain province, Jurassic age				
113. Lower Sunnyside seam (hvBb), Columbia mine, Coleman, Alberta, Canada	5.9	19.13	1.222	0.4951
Pacific Coast province, Eocene age				
137. Unnamed seam (lig), Alpco quarry, Amador County, Calif.	12.1	19.24	1.211	0.4886

The reported isotopic compositions of gasoline lead additives (Fig. 1) show that they were manufactured with lead ores ranging from pre-Cambrian to Tertiary age (*7*). For example, the Bangkok and Hong Kong gasoline leads are typically of pre-Cambrian origin and were probably mined at Broken Hill, Australia. The Amsterdam and San Francisco gasoline additives also contain appreciable amounts of pre-Cambrian leads, mined in Australia and Idaho, respectively. The computed ages of gasoline leads in other cities of the United States and Europe range from Paleozoic to Tertiary.

By comparing the isotopic composition of the lead in North American coals with that of the lead in gasoline additives, we find that, except for coal 101 and the Houston gasoline, there is a distinct difference between these two sources of lead pollutants. The Houston gasoline contains some anomalous J-type lead, which is characteristic of the Mississippi Valley lead ore, and coal 101 is from a Montana coal mine that is not a major producer. Therefore, it is practicable to distinguish between gasoline and coal leads by examining their isotopic compositions (*8*).

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8. We consider that a statement from one of the reviewers of this report is worth quoting. The reviewer commented that "it would be a good idea for tracer purposes if the [lead additive manufacturer] were to use just southeast Missouri or even better just Coeur d'Alene/Sullivan lead to permit the lead to be accurately traced since both of these series of deposits have rather unique lead isotopic compositions compared to surface sediments."
9. We thank numerous coal mines for their cooperation in providing the specimens and C. Snyder for technical assistance. Supported by the Environmental Protection Agency and the National Science Foundation.

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