Depletions of 0.2 to 0.6 percent are found at 30 cm for K^+, increasing further with depth (except at station D) (*13*).

We have also analyzed for Na^+ and Mg^{2+} but have found that NH_4^+, present in some marine sediments, affects our results. These data have not been reported in the face of this uncertainty. The Ca^{2+} and K^+ results are not subject to significant interference by NH_4^+.

These changes in interstitial K^+ differ quite markedly from those reported previously in studies of core sample extracts. Whereas earlier investigations of the upper few meters of pelagic sediments with few exceptions have shown K^+ enrichment, relative to ocean waters, in the pore fluids (*2 3, 14*), we have found K^+ depletion in all of our in situ samples from such sediments. This difference might have been anticipated since the enrichments previously reported can, in almost all cases, be attributed to temperature-induced artifacts.

The sediments we have sampled differ widely in their environment of deposition, suggesting that K^+ depletion in interstitial solutions is widespread and perhaps generally characteristic of pelagic sediments in the North Atlantic. The pore water studies of the Deep Sea Drilling Project provide supporting evidence for the uptake of K^+ in most pelagic sediments (*15*). It was found that the K^+ concentration most commonly decreases with depth in the sediment. Those data were derived from pore water samples collected over depth intervals of several hundreds of meters in a variety of sediment types, revealing long-term trends in sedimentary reactions. The in situ data reported here indicate that this K^+ uptake is already under way even in the youngest, uppermost sediments.

The Ca^{2+} enrichments we find in the upper meter of sediment in all of the oceanic sediment profiles thus far determined are considerably larger than those previously observed in piston core studies. These enrichments probably result from the dissolution of $CaCO_3$. The bottom waters at these sites are almost certainly undersaturated with respect to skeletal calcite in the sediments, and Ca^{2+} enrichment through solution is to be expected (*16*). The decrease in Ca^{2+} with depth, seen at four of the five sites, may be the result of bacterial oxidation of organic matter and the consequent increase of interstitial HCO_3^-. However, definite conclusions regarding this hypothesis require additional data on HCO_3^- and SO_4^{2-} concentrations.

The gradients of interstitial Ca^{2+} and K^+ observed by means of in situ sampling are such that, if widespread over the rest of the world ocean, they could produce diffusive fluxes that are comparable to the annual inputs of these ions by the rivers of the world. In the case of Ca^{2+}, the upward diffusive flux merely returns a part of the great downward flux of particulate $CaCO_3$. In the case of K^+, the downward flux is in the direction required to balance river input.

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Heavy Elements in Surface Materials: Determination by Alpha Particle Scattering

Abstract. *The backscattering of alpha particles from a radioactive source can be used to determine the amounts of heavy elements such as lead in surface materials. A light, portable instrument has been constructed that can be used as a survey meter for painted surfaces. It has a sensitivity of 0.3 percent by weight in a measurement of a few minutes.*

Concern about lead poisoning in young children has led to interest in portable instruments that can detect lead in paints used in dwellings and children's toys (*1*). Currently, most city housing and health codes limit the lead content of surface coverings to 0.5 percent by weight (*2*).

It has been shown (*3*) that the elastic scattering of alpha particles can be used for quantitative elemental analysis of surface materials. This technique was successfully applied in 1967 and 1968 to obtain, by remote control, the first chemical analyses of the lunar surface (*4*). We now report the feasibility of using this technique to determine the amounts of heavy elements in surface samples with a simple portable instrument. The demonstration instrument was constructed by using techniques and many parts that were developed for the Surveyor lunar program.

In this method the determination of the amounts of heavy elements in surface materials is based on conservation of momentum and energy when an alpha particle is scattered by a nucleus of mass A. The quantitative energy relation in the backscattering of alpha particles is:

$$\frac{T_m}{T_0} = \left(\frac{A-4}{A+4}\right)^2$$

where T_0 is the initial energy of the alpha particles and T_m is the maximum possible energy after scattering from a nucleus with an atomic weight A. The alpha particles scattered from a thick sample will normally have a continuous energy spectrum extending down to zero energy. However, an electronic threshold can be set so that an instrument registers only alpha particles with energies greater than some preset value, T^*. Such alpha particles can arise only by scattering from chemical elements with atomic masses, A^*, greater than

$$A^* = 4\left[\frac{1+(T_m^*/T_0)^{1/2}}{1-(T_m^*/T_0)^{1/2}}\right]$$

In this way, the system becomes insensitive to elements lighter than some critical element A^*, the mass of which can be selected by the appropriate electronic threshold. In addition, the intensity of the backscattering increases rapidly with the atomic number Z (approximately as $Z^{2/3}$). As a consequence, the sensitivity of the method is highest for the heavy elements that are of interest in the applications being considered.

On the other hand, the difference between the maximum energies of alpha particles scattered by elements with adjacent atomic numbers decreases with increasing mass number. Thus, the determination of heavy chemical elements by this method is in terms of groups of elements. This lack of discrimination has advantages as well as disadvantages. Most heavy elements such as lead, mercury, and thallium are poisonous. Measurement of all of these together will often be useful in a survey instrument.

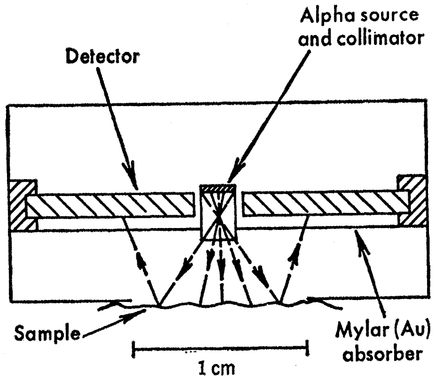

Fig. 1. Alpha-scattering detector for heavy elements: diagram of operation.

Another characteristic of the method is that it provides information only about the top layer of the surface. In the instrument described here this is a depth of only a few micrometers. Thus, only the top layer of a surface coated with many layers of paint is examined, unless the lower ones are uncovered.

An instrument based on these principles has been designed and constructed. It was intended to demonstrate the practicality of a small portable instrument for use as a survey meter for lead detection by a semiskilled person. It weighs about 2 pounds (0.9 kg), has a volume of about 1200 cm^3, has power provided by a 5-volt rechargeable battery, and draws less than 0.5 amp. It can detect a lead content of less than 0.3 percent in a surface paint in a measurement lasting a few minutes.

Figure 1 is a diagram of the operation of the instrument. The main components are:

1) A source of alpha radioactivity that emits relatively monochromatic alpha particles and a negligible amount of harmful penetrating radiation such as gamma or x-rays. The sensitivity of the instrument and, to some extent, its capability for distinguishing between adjacent elements depend on the quality of the source. The demonstration instrument uses 4 mc of ^{242}Cm [half-life, 163 days; alpha energy, 6.1 million electron volts (Mev)]. Curium-242, however, is not easily available, and its half-life is probably too short for a practical instrument. Fortunately, there are other sources of alpha radioactivity such as ^{244}Cm (half-life, 18 years; alpha energy, 5.8 Mev) and ^{238}Pu (half-life, 89 years; alpha energy, 5.5 Mev), which are probably more convenient to use.

2) A detector of the silicon surface-barrier type to register the number of backscattered alpha particles and their energy. In order to simplify the instrument and to achieve optimal geometry, a specially fabricated small circular detector with a hole in the center was used. This makes it possible to locate the alpha source in the center, the most desirable geometrical place. The active area of the detector is about 2.0 cm^2, its sensitive depth is 100 μm, and it operates at a bias of 5 volts.

3) Electronics consisting of a charge-sensitive preamplifier and amplifier for

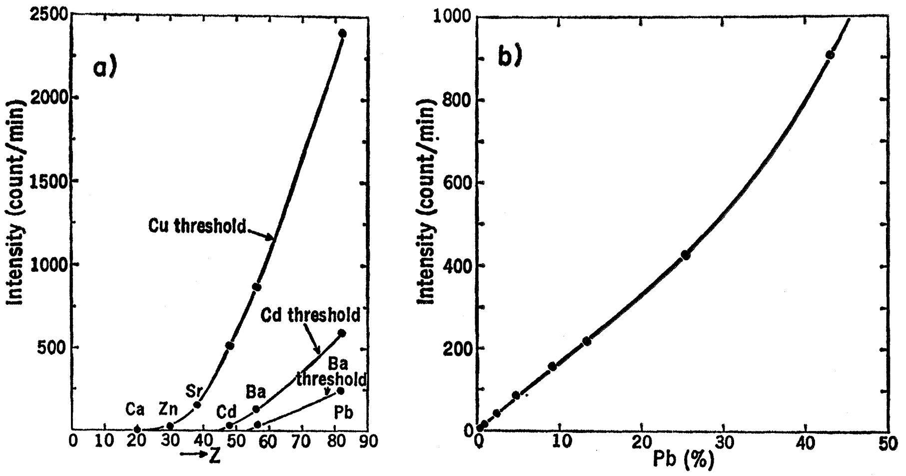

Fig. 2. (a) Response of the heavy element detector when measuring some carbonates at three different settings of the threshold. (b) Calibration curve for the low-level mode of the heavy element detector. The abscissas show the lead contents as percentages by weight giving rise to the intensities shown by the ordinates. The intensity is the number of backscattered alpha particles per minute above the threshold.

the signal from the detector, and a discriminator eliminating the signals from the alpha particles with low energies. A variable discriminator control makes it possible to select the lightest element to which the instrument is sensitive.

4) Readout system and timer. Each alpha particle entering the detector with an energy above the set threshold is counted by a high-speed decade counter with an integrated circuit and internal memory. The total number of registered alpha particles is displayed on demand on a four-digit light emitting diode display system. A timer built into the instrument automatically stops the measurement after a desired time period.

A practical instrument should be operable in air. Because of the low penetrating power of alpha particles this requires that the distances from source to sample and sample to detector be as small as possible. This is achieved in the design illustrated in Fig. 1. The source is collimated in such a way that it irradiates an area of the sample which is small (about 1 cm^2), but large enough to minimize effects of surface inhomogeneities in the sample. The overall geometry was selected to maximize the solid angle for detection of alpha particles without appreciably degrading the resolution of the instrument by including too large a variation in scattering angle.

Spectra of backscattered alpha particles obtained in a vacuum from pure elements have sharp end points at high energies (*3*). In air the particles lose energy, and the end points are shifted to lower energies and are less sharp. They are, however, still defined well enough to allow a threshold to be set for a particular element.

Figure 2a shows the integrated response of the instrument when examining some carbonates, with three different settings of the threshold. With the lowest threshold the instrument registered alpha particles scattered from all elements heavier than about zinc. The sensitivity of the instrument is high, and lead present even in about 0.1 percent by weight can be detected in a short time in this mode. In the other two cases in Fig. 2a the threshold was set for cadmium and barium.

Most tests with this instrument were made with only two thresholds: low level (set to detect elements heavier than zinc) and high level (set to detect elements heavier than barium). The background in the low-level mode was about 2 counts per minute; in the high-level mode it was less than 1 count per minute.

Table 1. Lead contents in paints on some toys; the results obtained with the instrument described here are compared with the results of conventional analysis (*5*). The measurement time with the alpha detector was 1 minute.

Sample	Lead (% by weight)	
	Alpha scattering heavy element detector	Conventional analysis
1	<0.1	0.08
2	0.1	0.3
3	12, 14.5	17.0
4	4.3	3.5
5	0.6	0.87
6	0.25	0.42
7	<0.1	0.09
8	19	23

The instrument was calibrated (for amounts of heavy elements as percentages by weight) by using a set of paint samples with known amounts of lead ranging from 0.2 to 43.0 percent. Figure 2b shows a calibration curve for the low-level threshold setting. The calibration curve for the high-level setting is similar except for the lower response rate. The response, although interpretable as lead content through the calibration curves, refers, strictly speaking, to the total heavy element content, with a relative sensitivity determined by Fig. 2a.

As a part of the testing of the performance of the instrument, the paints on a number of children's toys (*5*) were surveyed for lead content. Table 1 compares the results obtained with this instrument with those obtained by conventional analysis. This table indicates that measurements made in 1 minute by such an instrument can determine the lead contents of paints in practical situations. As mentioned earlier, the painted surface being examined must be bare; for example, a wax or varnish covering ½ μm thick will decrease the sensitivity for lead by about a factor of 2.

An instrument of the type described here could have many other applications in surface analysis. It would provide relatively rapid, nondestructive measurements of the quality of gold or platinum, and of the thickness and uniformity (in the micrometer range) of certain surface coatings and thin films. Relatively minor modifications could lead to devices for measuring gas densities.

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Huntite Flowstone in Carlsbad Caverns, New Mexico

Abstract. *Huntite flowstone has recently been discovered in Carlsbad Caverns. This flowstone occurs as a thin, white layer of microcrystals (approximately 1 to 60 micrometers in diameter) which appears buckled and crinkled. The huntite is believed to be precipitating directly from magnesium-rich solutions rather than forming by alteration of preexisting minerals.*

Carlsbad Caverns is well known for its abundance and diversity of carbonate speleothems (*1*). Reported secondary carbonate minerals are calcite, aragonite, dolomite, hydromagnesite, and huntite (*2*). Huntite, $CaMg_3(CO_3)_4$, is a rare mineral found previously in caves as moonmilk (*3–5*), and elsewhere in cavities and vugs of magnesite, dolomite, and deweylite (*6*) and in marine evaporites (*7*).

Recently, huntite has been discov-