Reports

X-ray Fluorescence: Detection of Lead in Wall Paint

Abstract. *An instrument has been developed for the in situ determination of lead on painted surfaces. It utilizes, as a source of gamma rays, radioactive cadmium-109 and its daughter silver-109 (metastable) to excite the K series x-rays of lead, and a solid-state, lithium-drifted germanium detector. The device, which is capable of detecting 0.26 milligram of lead per square centimeter of paint* [*approximately 3 percent (by weight) of lead in a single coat*] *beneath ten layers of lead-free paint, has been tested in a preliminary survey of several tenement apartments in New York City.*

One of the serious public health problems today is the occurrence of lead poisoning in children who live in tenement buildings in large cities (*1*). The most probable cause of the disease is the ingestion of lead paint, which was used when these buildings were new.

This hazard may be eliminated either by removing the paint or by providing a durable and permanent covering for the paint. However, the economical and effective approach to decontamination has been hampered by the lack of a rapid and sensitive method for the detection of lead paint on wall and woodwork surfaces. In this report we describe a portable instrument which makes possible a nondestructive, in situ determination of lead on painted surfaces. Use of this instrument will permit the quick examination of apartments where a hazard from lead paint is suspected.

The prototype system constructed for this study is composed of two sections: (i) the detector section, which consists of a preamplifier and a Ge(Li) detector attached by way of a coldfinger to a cryostat containing 3.5 liters of liquid nitrogen with a holding time of 3 days; and (ii) the electronics module, which consists of an amplifier, a single-channel analyzer, a scaler, and a bias power supply for the detector. Each section weighs approximately 20 pounds (9.1 kg) (*2*).

The operation of the device is based on the detection of the K series x-rays emitted by lead atoms when they are excited by the 88.21-kev photons of ^{109}Cd-^{109m}Ag (*3*). The collimated excitation source is attached to the cryostat next to the detector. The excellent resolution of the Ge(Li) detector separates the 66-kev backscatter peak almost completely from the 84.92-kev lead K_β x-ray used for the determination of the amount of lead on the surface. Initial experimentation with other detectors [NaI(Tl) scintillation and gas proportional] showed that this separation was necessary since the amount of backscatter and hence the background was found to be dependent on the type of backing material on which the paint is placed. The Ge(Li) system shows a constant (5.0 ± 2.5 count/min) background regardless of the type of backing materials used. The spectrum of ^{109}Cd backscatter in relation to the Pb K_α and K_β x-rays is shown in Fig. 1.

Table 1. Instrument results and chemical analyses of calibration panels and field core samples.

Sample	^{109}Cd (count/min)	Lead	
		mg/cm^2	Percentage, weight per weight
		Panel cores	
1	10.6	0.19	0.17
2	14.0	0.52	0.40
3	16.4	0.52	0.52
4	35.0	2.96	2.28
5	64.8	4.34	3.62
6	66.6	3.34	3.34
7	210.0	13.07	10.89
8	246.0	17.52	12.51
		Field cores	
9	12	0.14	0.13
10	56	6.38	4.25
11	96	18.57	4.19
12	92	12.97	4.30
13	12	0.44	0.28
14	82	7.20	3.13
15	13	0.24	0.20
16	70	6.77	2.82
17	29	2.24	1.25
18	118	11.00	4.42
19	20	0.24	0.20
20	9	0.24	0.20
21	118	19.40	4.98
22	11	0.12	0.16
23	154	22.50	6.43
24	51	6.35	1.99
25a		0.69	0.31
25b	78*	7.29	6.08

* Core sample upon removal was cleaved into two layers: the surface layer is sample 25a and the base layer is sample 25b.

Three separate methods have been used in calibrating the system. (i) Sprayed paint samples of known composition were provided by the Lead Industries Association, Inc.; (ii) a set of mock wall panels was constructed and painted; and (iii) an apartment was examined (field samples). In cases (ii) and (iii) samples were removed by a coring technique and analyzed chemically. The panels were built to represent wall surfaces and had both wood lathe and metal lathe backing covered by plaster cement and plaster. These panels were painted with single coats of lead paint with the following compositions (in percent by weight): 2.5, 14, and 64, with the lead paint located at either the bottom, middle, or top of ten other coats of nonleaded, titanium-based paint. With this arrangement it is possible to ascertain the response of the detector to increasing amounts of lead and also the degree of absorption below several layers of other paints. Gypsum wallboard and wood were also used as background comparisons against unpainted sections of wood lathe and metal lathe panels.

Core samples from the apartments were taken from the same spot on the wall at which the lead determination had been made with the instrument. The results of chemical analysis of the test panels and apartment sample cores are shown in Table 1 along with the results for the instrument. The amounts of lead detected are given in milligrams of lead per square centimeter of paint and in percentage (weight per weight). The instrument response is proportional to the total amount of lead present in the excited area and is largely independent of the total amount of overlying paint. Thus the response is directly related to the weight of lead per unit area. In most published reports and in the health codes relating to this problem percentage by weight has been used as a measure of the lead concentration. The presence of several thick layers or of numerous thin layers of lead-free paint will result in lower percentages (by weight) of lead without actually reducing either the amount present or the effective health hazard. The amount of lead ingested by a child is independent of the overlying material, and the hazard, for the most part, is related to the amount of lead ingested,

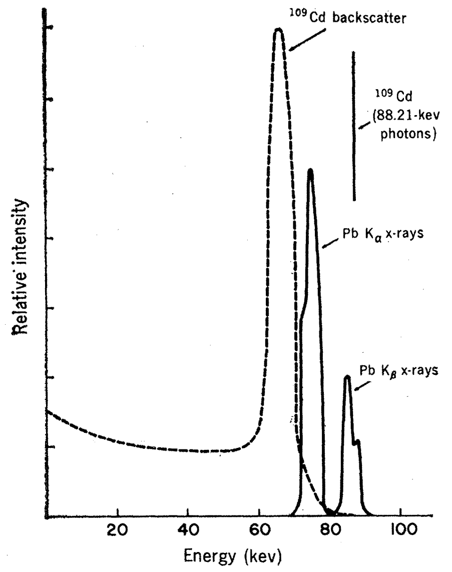

Fig. 1. Backscatter of ^{109}Cd-^{109m}Ag and the K series x-ray spectrum of lead measured with a Ge(Li) detector.

not to its percentage by weight with relation to the remaining innocuous material.

The results are also shown in Fig. 2, where curve A represents the response of the detector to the test panels and curve B is the field response. The difference in slope between the test panel response and the field sample response is believed to be due to increased self-absorption of the x-rays when several layers of lead paint are present and to increased absorption as the number of coats of overlying nonleaded paint increases to 20 layers or more. An electron microprobe scan performed on one paint chip removed from a kitchen wall showed two layers of lead paint at the back of the chip, with three or more coats of lead paint toward the center, these in a chip 2260 μm thick containing well over 25 coats of paint altogether (*4*).

In one field sample it was noted that the layer of lead paint was located at or near the bottom of the coats of paint. Since lead-based paints have not been recommended for interior use since about 1940, these findings generally confirm what was expected.

The effect of increasing self-absorption due to several layers of lead paint is shown in Fig. 3, for which several of the sprayed paint samples were overlaid for each reading. These results indicate that, in the field, where it is impossible to ascertain how many coats of lead paint are present on a surface, the reading may underestimate somewhat the lead on the wall. However, the error is on the conservative side from the regulatory viewpoint, as the actual amount present will always be greater than that reported when the absorption effect is significant. Calculations based on the amounts of lead in the calibration panels indicate that the prototype instrument is capable of detecting 0.255 mg/cm^2 or approximately 3 percent (by weight) of lead in a single layer of paint beneath ten lead-free layers (titanium-based) in a 1-minute determination.

Table 2. Frequency of contamination.

Source of paint sample	Number of samples	Percentage of samples with lead content of ≥ 5 mg/cm^2	≥ 25 mg/cm^2
Apartments	8	100	75
Rooms	49	81	49
Wood	49	76	41
Walls, total	87	44	17
Kitchen and bath	31	68	19
Bedroom	39	64	31
Living room and dining room	14	21	0

To further test the use of the instrument, a survey was made of eight apartments in three buildings in one of the "lead belt" areas of New York City. Table 2 shows the results of a frequency analysis of the data from these apartments. The apartments and rooms are classified according to the highest concentration of lead found in them, whether this was a wall, a door, or a doorframe. Generally, more than one high value occurs in the case of any given apartment or room. These results indicate that the lead paint may be found anywhere, although not on all painted surfaces. The most frequent instances of lead contamination have been found on wood surfaces and on

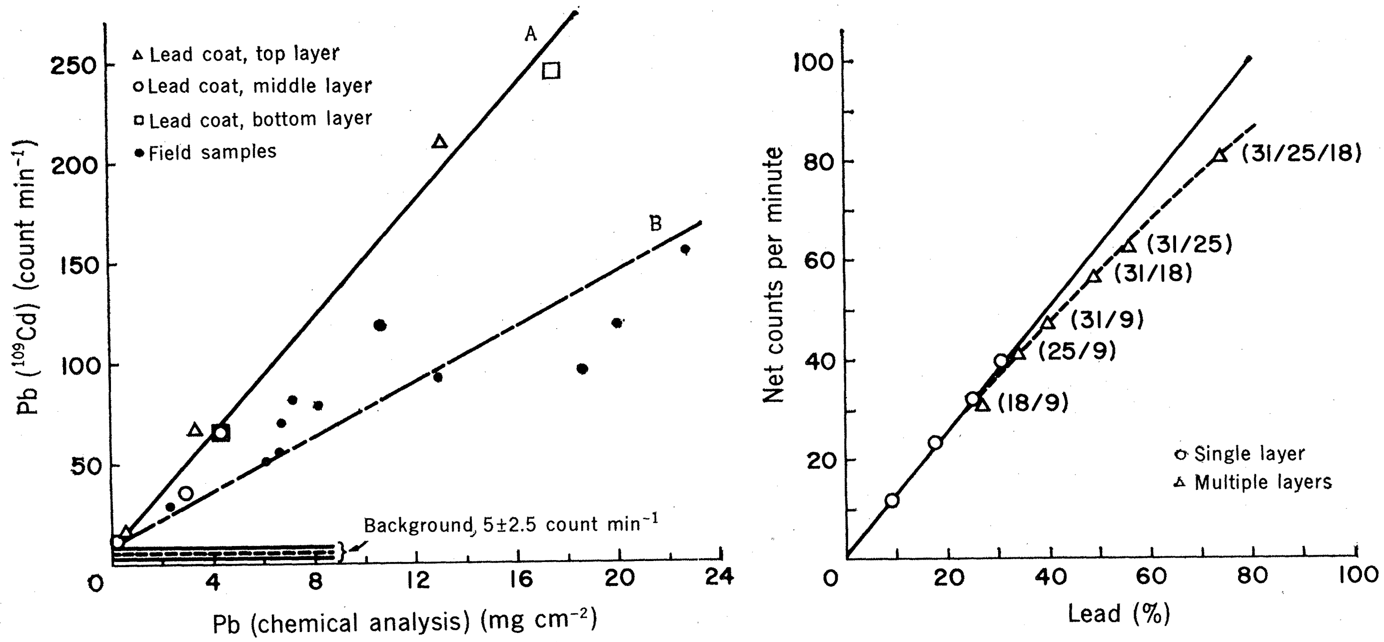

Fig. 2 (left). Amounts of lead detected by the ^{109}Cd system versus amounts detected by the chemical analysis of field samples. Curve A, standard panels; curve B, field samples. Correlation coefficient for curve A, 0.99; correlation coefficient for curve B, 0.94. Fig. 3 (right). Self-absorption effect of multiple layers of lead paint. The parenthetical numbers represent the percentages of lead in the successive layers of paint (percentage in the topmost layer is given first).

bedroom, kitchen, and bathroom walls. The highest amounts of contamination have generally been observed on wood surfaces, that is, doors or window frames. None of the apartments studied was found to be uncontaminated (*5*).

An evaluation has been made of the dose rate at various positions while the instrument is in operation to ensure that there is no radiation exposure hazard to either the operator or apartment occupant from its use. The operational doses at the distances indicated are as follows: (i) 6 inches (15.2 cm) directly in front of the uncapped source, 25 mr/hr; (ii) 6 inches directly in front of the capped source, background; (iii) 12 inches from the wall surface with the instrument in the operating position against the wall surface, 0.03 mr/hr; and (iv) at the surface of the hollow, wood-lathed, plastered wall directly opposite the source, that is, transmission through the wall with the least amount of attenuation, 0.25 mr/hr.

Since the source is uncapped only when it is pointed at a wall surface, exposure condition (i) is expected not to occur in practice with the instrument in the hands of a trained operator. Condition (iv) is unlikely to occur, but may be considered the "worst possible condition" as far as the apartment occupant is concerned. A 2-minute exposure at this position would produce a total exposure of $0.25 \times 1/30 = 0.0085$ mr. Radiation protection guides in current use allow a cumulative exposure of 500 mr for 1 year to an individual (*6*). An exposure of 0.0085 mr is a negligible fraction of this total. The exposure due to backscatter (0.03 mr/hr) to the operator is also well below radiation exposure limits for occupational exposure.

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References and Notes

1. H. Jacobziner, *Clin. Pediat.* **5**, 277 (1966).
2. A second-generation design (now available from Canberra Industries, Inc., Middletown, Conn.) contains the detector, cryostat, and electronics in a single module weighing between 15 and 20 pounds.
3. J. R. Rhodes, "X-ray Analysis Using Radioisotope Sources" [*U.S. At. Energy Comm. Res. Develop. Rep. ORO-3224-14* (1968)].
4. L. L. Ciaccio, personal communication.
5. G. R. Laurer, T. J. Kneip, R. E. Albert, F. S. Kent, in preparation (the statistically designed, random-sampling program to be described here provides a frequency analysis of the contamination, with confidence statements on the degree to which the results represent the overall community).
6. *Fed. Radiat. Counc. Rep. No. 1* (1960).
7. We thank Profs. M. Eisenbud and N. Nelson for their advice and guidance, C. Strehlow and J. Miller for help in the chemical analyses of the paint samples, and the personnel of the New York City Department of Health for their aid in finding an apartment house for the field test and for help in the removal of core samples. This work was supported by grant U-2078 from the Health Research Council of New York City and is part of a New York University Medical Center program supported by the Public Health Service, Division of Environmental Health Sciences, National Institutes of Health, under grant ES-00260.

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Final Desiccation of the Afar Rift, Ethiopia

Abstract. *Stable and radioactive isotope studies of ancient corals and mollusks from a fossil atoll in the Afar Rift indicate that final separation of the Afar Depression from the Red Sea occurred not earlier than 32,000 years ago. Desiccation followed within a few thousand years. The events recorded in the Afar Rift illustrate the processes occurring in the incipient stages leading to the formation of an oceanic body by rifting of a continental block.*

The geology of the Afar Depression of Ethiopia is of great interest because it may elucidate the processes that take place during the earliest stages of the formation of an oceanic body by rifting of a continent. The northern part of the depression, as much as 120 m below sea level, is an elongated rift located between the Ethiopian Plateau and the Red Sea (Fig. 1). Between the depression and the Red Sea lie the Danakil Alps, an ancient continental block that was originally part of the Ethiopian Plateau. Separation of the Danakil Alps from the plateau by tensional and rotational movements (*1*) created the depression. As a consequence of these motions, continental crust is missing below the axial zone of the northern Afar Rift (*2*). The depression was an intermittent marine basin until late Pleistocene time (*3*), when it last became severed from the Red Sea, probably by newly formed volcanic structures in the Gulf of Zula area. Final desiccation followed. In this report we attempt to date these events.

During recent expeditions to Afar (*4*), a series of originally submarine volcanoes were discovered (*5*). Among them is a volcanic cone about 50 m high and 500 m wide. This structure, located in the axial zone of the rift at about 13°20′N and 41°00′E (Fig. 1), may be considered a fossil atoll, since it consists of a ring of submarine basaltic pyroclastics capped by molluscan deposits and a well-preserved coral reef. The fossil organisms were evidently living during the time between cessation of volcanic activity and desiccation of the depression. Stable O and C isotope analyses of calcium carbonate from these organisms were done to study the progress of desiccation. Age determinations were made by C^{14} and Th^{230}/U^{234} methods. Procedures and assumptions pertaining to the latter method have been given by Thurber *et al.* (*6*) and Osmond *et al.* (*7*), among others. Results are shown in Table 1.

Sample M-8A, a large pelecypod (probably of the genus *Tridacna*), consists of an outer portion, which is almost pure calcite (M-8A$_2$) clearly derived from recrystallization of aragonite, and an inner zone, which is pure aragonite (M-8A$_1$), as determined by x-ray diffraction. Stable O and C isotope analyses and C^{14} dating were performed on both the calcitic and aragonitic parts.

Sample M-8B, a coral probably belonging to the genus *Astracosmilia*, also showed some evidence of recrystallization of calcite from aragonite, but the two crystalline phases could not be physically separated for analysis. This sample was analyzed for both Th and U and for stable O and C isotopes, but not for C^{14} dating.

The O^{18}/O^{16} and C^{13}/C^{12} analysis of the aragonitic, unrecrystallized mollusk sample M-8A gave values that indicate a normal marine environment (Table 1). The recrystallized calcitic portion of the same mollusk (sample M-8A$_2$), on the other hand, gave an O^{18}/O^{16} composition of +12.2 per mil, which indicates recrystallization in a hypersaline environment. If the relationship between O^{18}/O^{16} composition and salinity discussed by Craig (*8*) obtains, the salinity of this environment can be calculated to have been about 75 per mil. The O^{18}/O^{16} composition of the coral (sample M-8B) is about 5 per mil heavier than usual in unrecrystallized corals (*9*), obviously a result of the