The Determination of Lead in Paint Films with a Portable Isotope Fluorescence Analyser

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Although there are numerous environmental sources of lead of significance for children (1) the major lead hazard in most urban populations is domestic paint (2). Conventional lead screening programs have previously been focussed on the child rather than his environment and so detect only those children who have accumulated a sufficient body burden of lead to render the tests positive. Although such programs have shown an annual poisoning rate of 0.5% among children at risk (3) they fail to identify those dwellings that are potential hazards for children not yet exposed. Chemical analysis of paint from surfaces accessible to children have shown that a wide range of lead contents may be present in homes of varying age and social status (4). Paint sampling in this way has disadvantages in that the subsequent analysis is relatively time consuming and costly and that the painted surface must be damaged so that a representative full-thickness sample may be obtained.

The portable isotope fluorescence analyser has long been used by geologists for the determination of the mineral content of ores but has not previously found application in this field. The apparatus is based on the principle of x-ray fluorescence and has the advantages that it is portable and that it can be applied repeatedly to any surface without damage. Preliminary studies have suggested that the device might find application in the determination of lead in domestic paint films in situ. In this paper the apparatus and its application to the analysis of paint films both in the laboratory and in the domestic environment are described.

Apparatus

The device employed was the Portable Isotope Fluorescence Analyser manufactured by Rank Precision Instruments Ltd., London, England. It comprises a portable battery-powered ratemeter which is conn-

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ected by means of a flexible cable to a probe unit for application to the test surface. The combined weight of the assembly is 7.58 kg. The probe unit contains a radioactive source (plutonium 238, 30 mCi) sealed in an aluminium capsule. This is shielded when not in use by means of a swivelling shutter which is displaced only when the unit is being applied to the test surface and a safety lever simultaneously operated. The surface radiation from the instrument when not in use is less than 0.2 mrad/h and thus presents no hazard to the operator. The radiations emanating from the source which excite a fluorescent x-radiation from the atoms of the test material, are uranium L X-rays of 12-17 keV, which penetrate to an effective depth dependent on its composition, but seldom exceeding 2-3 mm. The fluorescent emission arising from the surface enters the probe unit through the terminal circular aperture surrounding the source and after passing through one of a pair of balanced filters is detected and measured by means of a conventional sodium iodide crystal and photomultiplier assembly housed in the probe. The balanced filters contain gallium or germanium and are devised such that they cut off emissions above and below the characteristic lead emission at 1.175 Å. Given suitable standards, the effective lead content of a material can thus be determined from the difference between the count rates obtained when the filters are deployed consecutively.

Standardisation

The observed difference in count rates for a given element will vary according to the matrix in which the element is dispersed. Although a 100% reading can be obtained with a sheet of the pure element of sufficient thickness, the readings obtained with lesser concentrations will be impaired by internal absorption of the exciting or emitted radiations. Ideally a series of standards of known chemical composition would have to be prepared for each test situation so that a standard curve for difference in count rates against lead content could be derived. While this is impossible for an unknown paint sample, it is simply achieved for a given paint by standard additions of a lead compound to aliquots of a liquid sample from which uniform films may be prepared and dried to give a standard series.

In this study a commercially available white undercoat domestic paint containing approximately 1% lead was used as the standard base. To aliquots of the paint, increasing weights of lead oxide (Pb_3O_4) were added and thoroughly mixed such that a series of paint films of lead content in the range 1-31% were obtained. Subtraction of the reading due to the lead content of the base paint allowed the construction of a calibration curve for the range 0-30%, the maximum reading was obtained by substitution of lead foil for paint to give 100% lead (Fig. 1). The readings obtained allowed

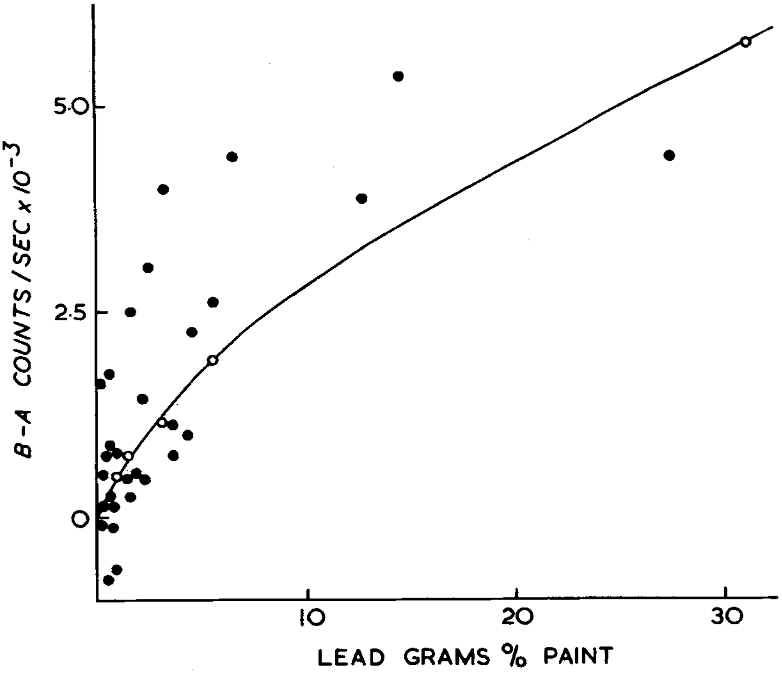

Figure 1. Count rate differences for paints of varying lead content a) laboratory prepared standards (open circles and curve) and b) domestic paint films in situ (closed circles).

determination of the lead content of a given film in the range 0-5% to an accuracy better than ± 0.2%. It was found that foils of 0.002" thickness gave readings that did not differ from those obtained from the surface of a lead brick, so that the effective thickness for the pure element was probably less than this. Standard paint films were obtained by pouring equal weights of the prepared paint standards (6.5 g.) into Petri dishes of uniform surface area (64 cm^2) supported on a top-loading balance. The paint was allowed to cover the whole of the dish surface such that a relatively thick film of uniform depth was obtained. The standards were dried thoroughly and reweighed before use in order to determine the lead content per gram of dried paint film.

NON-HOMOGENEITY

Non-homogeneity of the test paint film may introduce difficulties in interpretation of the readings obtained and in some cases render it impossible to obtain a representative figure. In most situations this results from the successive application of films of different lead or matrix content to a given surface. In its simplest form this comprises a double layered film but in many field situations more complex films with multiple layers are encountered. A double layered film may produce anomalous results in two ways depending on which layer is superficial with regard to the analyser probe. A surface layer of high lead content will thus register a falsely high lead content for the whole film, conversely if the lead containing layer is deep, the overlying film of low lead content may impair the efficiency of detection. The usual situation in the field involves the second of these two situations in which the deepest layer of paint has the highest lead content.

In order to assess the effect of overlying films a series of standard paint films was prepared in Petri dishes as described above to contain 31% lead. After drying each film was covered with secondary films of increasing thickness of the base paint of low lead content (1.0% lead) such that each film weighed 8mg/cm^2 when dry. Successive observations showed a progressive decrease in the apparent lead concentration until this approached zero with a covering paint film of 77mg/cm^2 equivalent to 9 thinly brushed layers (Fig. 2).

FIELD TESTING

Thirty-four homes inhabited by families with children in the 1-5 age group were selected from a group of families previously studied (4). The selection was arranged such that there was a wide scatter of lead concentrations in the domestic paint to which the children had access. In each house a reading was obtained from a painted surface in the room usually occupied by the children, in most cases this was a window sill or door frame. The isotope

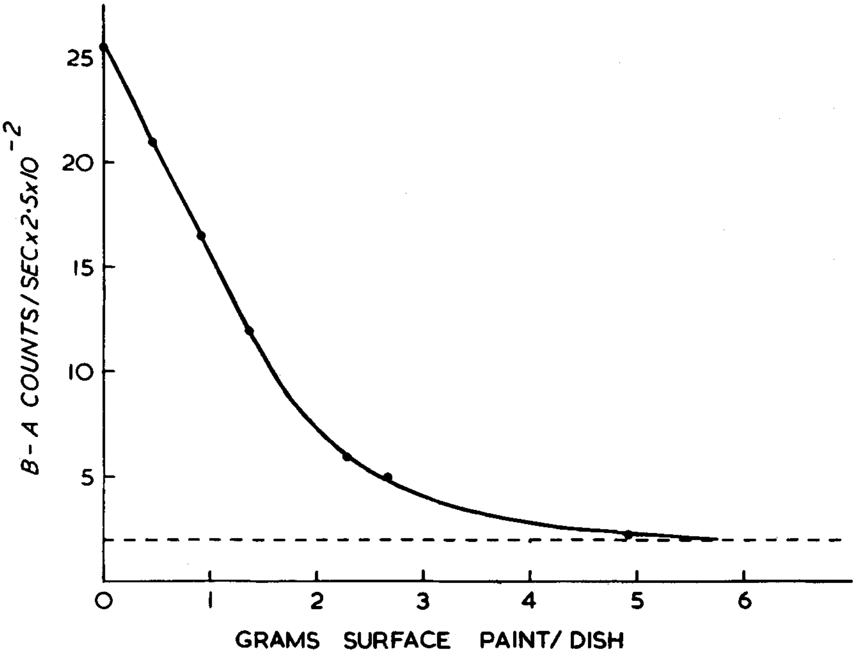

Figure 2. Graph showing the decrease in count rate difference for a paint containing 31 g% lead with successive applications of a second paint of low lead content (1.0 g%) in a dish of 64 cm^2. The interrupted line indicates the value obtained with the 1.0% lead containing paint alone.

fluorescence analyser was standardised in each home by means of a standard paint film previously prepared in the laboratory but in practice no appreciable change in machine performance occurred between home visits. Several readings were obtained from each surface to ensure that local variations in paint film thickness or lead content did not bias the results. After each series of readings a full thickness specimen of the paint film weighing about 50-100 mg. was obtained from the surface with the aid of a stainless steel scalpel blade. Chemical analysis of each paint specimen was made after wet digestion by means of a semiautomated alkaline dithizone method (6) and the results compared with the analyser readings.

FINDINGS

In general there was good correlation between the chemical and x-ray methods and the individual results are given in Figure 1. which also depicts part of the standard curve derived in the laboratory. Curve fitting of the data from the domestic paints together with statistical analysis was undertaken by means of a least squares program with an ICL 1950E computer and the derived curve together with 95% confidence limits are reproduced (Fig. 3). It is evident that the scatter of results was such that an apparent zero lead content could be obtained with the analyser in a paint film with an actual lead content of 5% and that conversely a count rate as high as 2.5X10^{3} cps could be obtained with very low lead concentrations. Similarly the wide separation of the 95% confidence limits require that a count rate of 3.0 X10^{3} cps before it could be inferred with that degree of certainty that the lead content of the paint film exceeded 1%, conversely such a count rate could equally indicate a lead content of up to 8%.

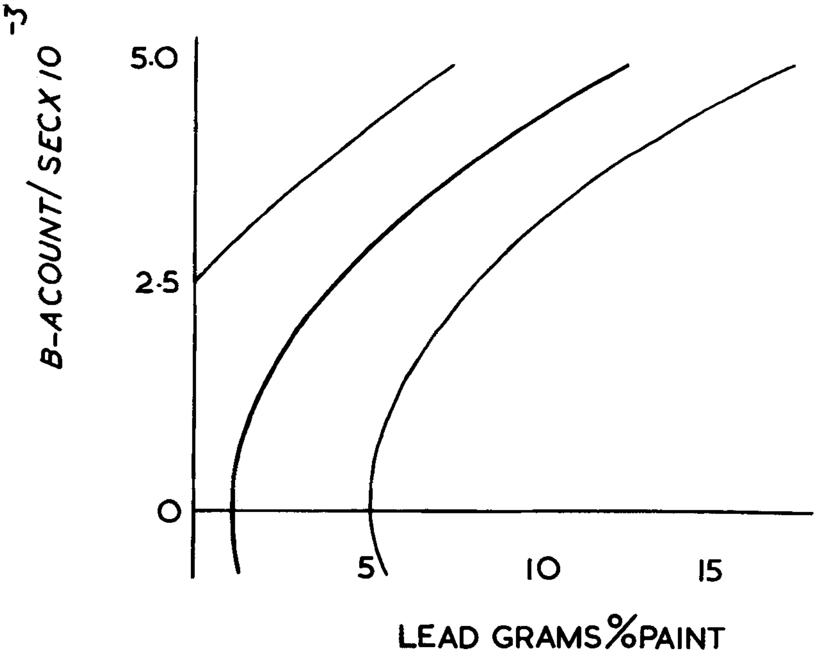

Figure 3. Best fit curve and 95% confidence limits for domestic paint film data with lead contents in the range 0-15%.

In its present form it is unlikely that this type of apparatus could find application in lead screening programs since it is incapable of discriminating between lead contents of domestic paint films in the 0-6% range. These findings are in marked contrast to the laboratory results for a series of standard paints and almost certainly result from the non-homogeneity and the variable thickness of paint films encountered in the field.

SUMMARY

The application of x-ray fluorescence to the determination of the lead content of paint films was evaluated using a portable isotope fluorescence analyser. Accurate determinations were achieved in the laboratory using prepared films in which the lead was dispersed through matrices of constant composition in a single layer. The presence of lead could be masked by overlying paint films of low lead content and was almost obscured by an overlying paint film of 77 mg/cm^2. The results for domestic paint films correlated with chemical analyses but the confidence limits were too widely separated to allow application of this technique to lead screening programs. The field results probably reflect non-homogeneity of domestic paint films.

Acknowledgements

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