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Determination of Lead in U.S. Dollar Paper Currency by X-Ray Fluorescence Spectroscopy

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The heavy metal lead has a serious influence on human health and exposure to this chemical element can cause environmental and occupational diseases (Fischbein 1992). The smelting of lead, its uses, and risks by adversely affecting various physiological and neurological systems have been known for many centuries and can be traced back to early human civilization. The poisonous characteristics of lead are exemplified by pewter, an alloy made in antiquity from tin (75% to 95%) and lead (25% to 5%). Lead can be leached out by liquids held in utensils made of pewter. Relatively minor uses of lead induce most of the adverse effects on health, and identification of the main mechanisms of exposure is much more important than reducing the total amount of lead in various products. The main application of lead is in electric batteries but a large proportion of batteries are recycled and therefore the dangers to the general population from lead in recycled batteries are greatly reduced. Human poisoning by lead is caused mostly by dissipative materials, such as paint and leaded gasoline, drinking water, dust and contaminated soil, which cannot be recycled. Lead-related legislation has been promulgated in many industrialized countries. The use of unleaded gasoline and unleaded pigments spread in western countries during the past decade, and had a direct effect on lowering the lead concentration in the blood of the general population (Richter and Fischbein 1992).

The aim of the present work was to study lead levels in the printing inks of U.S. dollar paper currency. Paper currency is an object of frequent daily use, and therefore contact with lead due to touching the notes is evident. Specimens were measured non-destructively by the X-ray fluorescence (XRF) method, which was employed due to the many advantages such as high selectivity and sensitivity, broad dynamic range, simultaneous analysis of most elements and no requirement for preliminary treatment of samples.

MATERIALS AND METHODS

A schematic drawing of the experimental system is presented in Figure 1. The X-ray tube is a water-cooled high-power tube that has a Mo anode and an optical point focus of 0.4 mm x 0.8 mm,

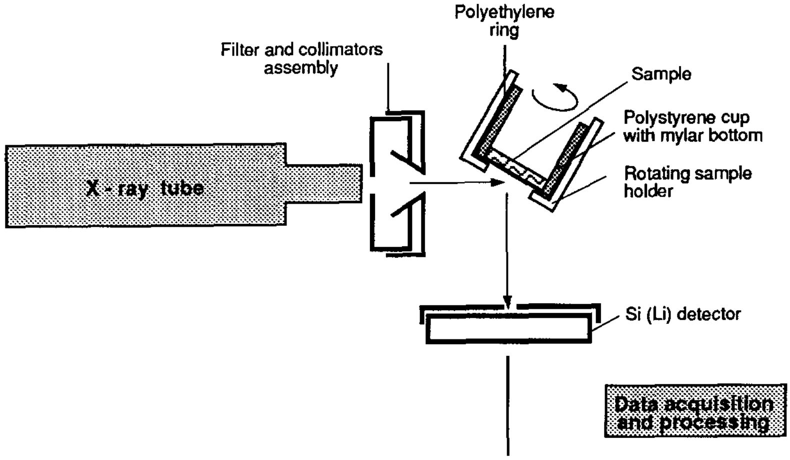

Figure 1. Experimental set-up

offering good geometry in the exposure of small samples. The tube was operated at a high voltage of 27 kV and a current of 30 mA, furnished by the 60 kV, 4.8 kW X-ray generator. Its 0.1% high voltage and tube current stability, offers good precision. A quartz filter between the X-ray tube and the sample, effectively eliminates the bremsstrahlung X-ray continuum emitted by the Mo anode. Therefore, the signal-to-background ratio was improved due to the nearly monoenergetic primary beam. The 3-mm-thick Si(Li) detector has an active area of 30 mm^2. A 12.7-μm-thick beryllium window on the cryostat enables the measurement of light elements, e.g. aluminum, where the X-ray energies are of the order of 1.5 keV. Collimators were used in the beams' paths with the aim of defining the cross section of the primary beam which exposes the sample and tailoring the secondary beam to decrease incomplete charge collection effects at the detector edges. These can have a detrimental influence on peak resolution. The energy resolution was 165 eV for the 5.9 keV Mn Kα line at a shaping time of 12μs of the electronic amplifier. Electronic pulses were analyzed and spectra processed by a Tracor Northern TN-5400 multichannel analyzer.

The lead content of U.S. bank notes was measured by placing the notes in the sample's position at an angle of 7° relative to the primary beam (see Fig. 1). In this counting configuration, the rotating sample holder and cup were removed. U.S. $ 100 bills of various printing dates were measured: 1934, 1963, 1969, 1974, 1977, 1981, 1985, 1988, 1990. The 1990 bill has an inner plastic security band. In all $ 100 bills, the same region was measured, viz., the mouth lips in the portrait of the American statesman and philosopher Benjamin Franklin. The bills were stretched planar before the measurement. Circular samples, 10 mm in diameter, were punched out from a $ 1 bill printed in 1988 and measured in polystyrene cups having 0.25-mil-thick mylar bottoms. Standard samples were prepared by pipetting a standard lead solution on the circle punched out from the $ 1 bill. Volumes of 12.5 to 50 μL were used and the liquids deposited were dried at room temperature. A 20.6 ppm lead standard solution was prepared by dissolving lead nitrate in distilled water. This conventional 'standard additions' technique was used to measure the lead content in the $ 1 bill.

RESULTS AND DISCUSSION

The XRF spectra of three U.S. $ 100 bills, printed in the years 1977, 1985 and 1990, respectively, are shown in Figure 2, as examples. The measurement times of these spectra were of the order of 300 seconds. In the 1977 bill, the main peaks detected in the spectrum were assigned to titanium, iron and lead. Identification of peaks was based on their energies and the known ratio between $K\alpha$ and $K\beta$, and $L\alpha$ and $L\beta$ XRF lines of an element. In the 1985 bill, the main peaks detected were titanium and iron, as in 1977. However, the lead $L\alpha$ and $L\beta$ peaks in the 1985 bill were much smaller than those in the 1977 bill. In the 1990 bill, titanium and iron were the main peaks detected, but the lead concentration was even lower than that of 1985. Minor peaks in the spectra were identified as chromium, manganese, nickel, copper, zinc, bromine and strontium. All the $100 bills of the years 1934 to 1977 were found in the measurements to have constant, high lead concentrations. Starting in 1981, the concentration of lead in the ink had been considerably decreased and this low concentration was measured in all the bills from the 1980s.

For quantitative purposes, measurements were normalized against the Mo peak. This broad peak (see Fig. 2) is composed of the 17.5 keV full energy of the Mo $K\alpha$ line and 16.9 keV X-rays. These latter rays are formed in the Compton scattering at an angle of 90^0 between the primary and secondary beams (see Fig. 1). Mo normalization is required because of the varying exposure conditions in the measurements and is a recommended procedure in quantitative analyses (Leyden 1984). By calculating the areas of the titanium, iron and lead peaks, and normalizing the areas of lead against titanium and iron, the following ratios were found:

Pb(1977)/Pb (1985) = 6±1 Pb(1977)/Pb(1990) = 250±150

Since the lead intensity in the 1990 bill is very low, the statistical uncertainty is very large and ratios of the order of 1500 can be found. The normalization of lead was based on the titanium and iron peak areas, which were found to be constant within ±20% over the printing time span.

The results of the 'standard additions' measurements, carried out with the dried aliquots of the standard lead solution and the circular specimens punched out from the $ 1 bill, are shown in Figure 3. Here, the net area of the Pb $L\alpha$ 10.55 keV peak was plotted <u>vs</u>. the mass of lead deposited on the circle. In these

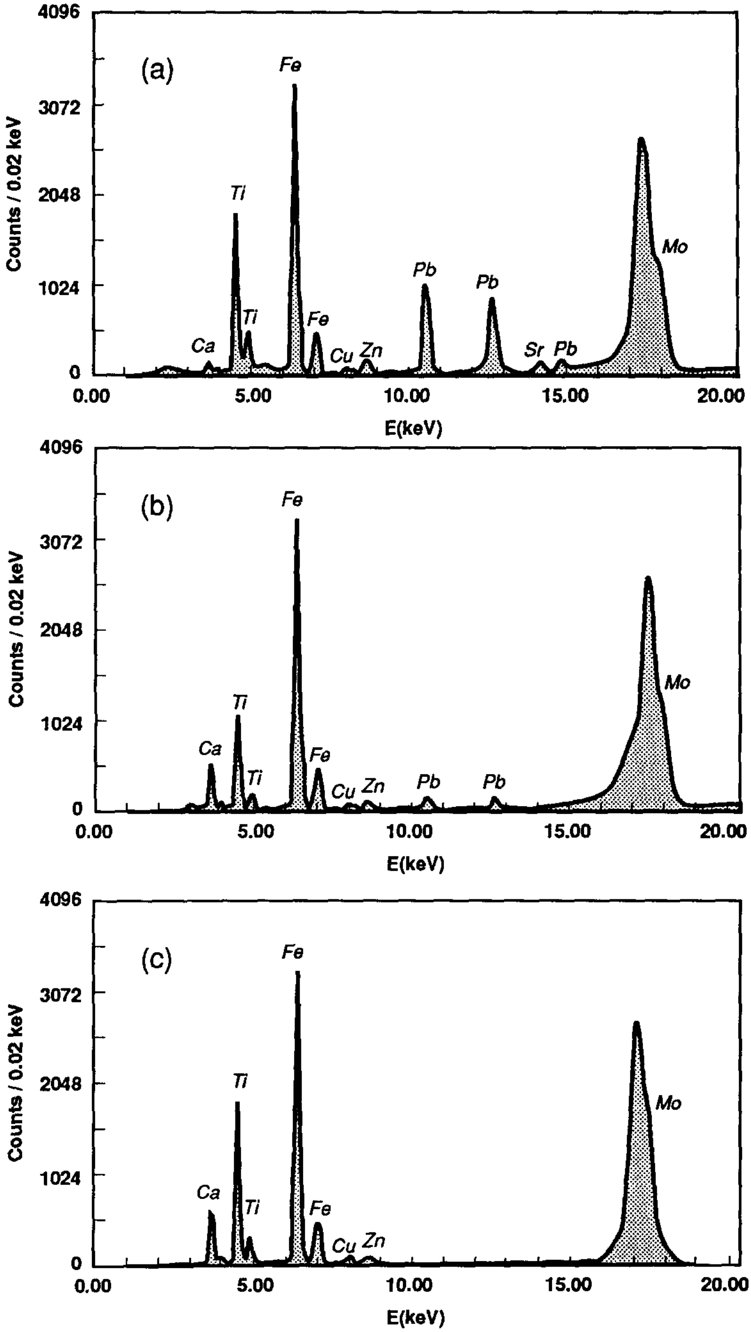

Figure 2. XRF spectra of $ 100 bills printed in:
(a) 1977; (b) 1985; (c) 1990

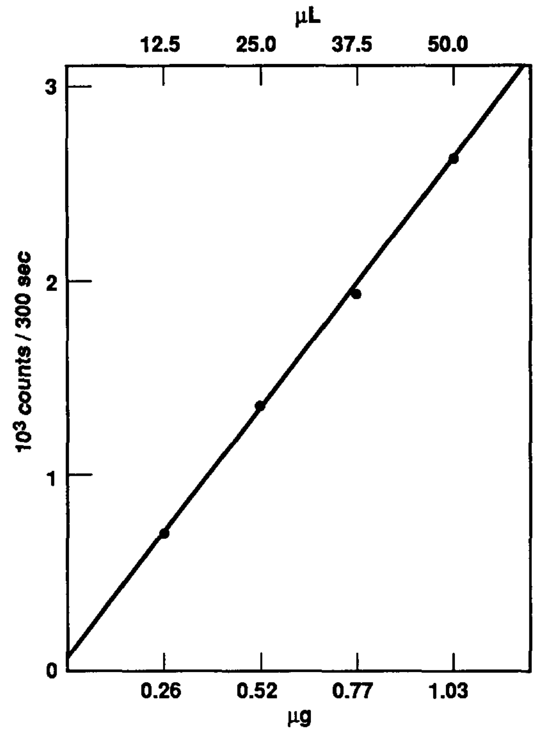

Figure 3. Lead Lα peak area <u>vs</u>. mass of lead

measurements each circle was counted for 5 minutes to achieve good counting statistics due to the low mass of lead. The equation of the straight line fitting the results in Figure 3 was obtained by linear regression. The intercept was 60.5 counts, the slope was 2482 counts/μg-Pb and the correlation coefficient was 0.9990. The intercept, corresponding to zero standard addition, is due to the lead content in a 10-mm-diameter circle of the \$ 1 bill, <u>i.e.</u>, 60.5/2482 = 0.024 μg = 24 ng. Direct measurements of three circular samples without standard additions, gave similar results. Since four different circles were used in the 'standard additions' measurements, the value of 24 ng refers to an average concentration defined over the four regions of sampling in the \$ 1 bill. In these regions, the colors of printing inks are green and black. Using the lead areal concentration of 24 ng measured in 1988, and the ratios of lead in various years, the concentrations in these years can be calculated.

A very high content of lead was discovered in a \$ 2 bill printed in 1976. Compared with the \$ 100 bills of that decade, lead was more abundant, by a factor of 2.8.

Lead was added to the printing inks as a 'metallic soap' to accelerate the oxidation reaction (Wolfe 1964). Oxidation is an important means of achieving ink drying and the 'metallic soaps' are used as oxidation catalysts, commonly called chemical driers.

The usage of lead soap was subsequently limited, due to the health risk (Bisset et al. 1979). Lead soap is now banned in the U.S. and recent articles do not mention it. The presence of titanium in the U.S. dollar bills can be explained by the filler used in the production process of the paper. The bills contain also a ferromagnetic pigment which can be found by commercial detectors; this pigment contains iron in the compound Fe_3O_4.

It can be concluded that U.S. dollar bills contained lead-based ink driers. Up to and including the printing year 1977, the areal concentration of lead was high compared with later printing years, and found to be of the order of 0.2 μg/cm^2. In 1981, and throughout the 1980s decade, the lead concentration was decreased by a factor of 6. In bills printed in 1990, an additional very significant decrease was detected, down to a value of approximately 0.8 ng/cm^2. This is an extremely low areal concentration, meeting the trend of reducing man's exposure to lead.

The health risk of lead in bank notes can be estimated quantitatively. Let us examine the case of a cashier exchanging U.S. dollar notes in an airport branch of a commercial bank. Let us assume the following: the area touched on one note is 10 cm^2; 1000 notes are touched per day; the ink drier fraction removed from the note to the cashier's fingers is 1%; The route of absorption in the body is by ingestion into the gastrointestinal tract and the fraction is 10% of the quantity on the fingers. Using the areal concentration 0.8 ng/cm^2 in recently printed notes, we estimate that the diurnal intake by ingestion is 8 ng, which is a very low value having a negligible significance to health, compared with the reported average dietary lead intake from 100 to 500 μg/day for adults (Elias 1985). The U.S. Food and Drug Administration (FDA) has estimated on the basis of 1982 data, lower values of the average daily intake of lead by consumption of food, water and beverages: 32 μg/day for adult females and 45.2 μg/day for adult males (EPA 1986).

A similar calculation for the old printed notes gave 2 μg/day, which is again lower than the reported or estimated values.

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REFERENCES

Bisset DE, Goodacre C, Idle HA, Leach RH, Williams CH (1979) The printing ink manual, 3rd ed, Northwood Books, London, England

Elias RW (1985) In: Mahaffey KR (ed) Dietary and Environmental Lead: Human Health Effects, Elsevier, New York, p 79

Environmental Protection Agency (1986) Air quality criteria for lead, Report No. EPA/600/8/83/028F, Springfield, VA: National Technical Information Service.

Fischbein A (1992) Occupational and environmental lead exposure, In: Rom WN (ed) Environmental and Occupational Medicine, 2nd ed, Little Brown and Company, Boston p 735

Leyden DE (1984) Fundamentals of X-ray spectrometry as applied to energy dispersive techniques, Tracor X-ray Inc., Mountain View, CA

Richter ED, Fischbein A (1992) Lead poisoning: II. Biological standards for occupational lead exposures - where do we stand now? Isr J Med Sci 28: 572-577

Wolfe HJ (1967) Printing and litho inks, 6th ed, MacNair-Dorland Co., New York