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METHOD OF XRF ANALYSIS FOR ENVIRONMENTAL Pb USING THIN FILM PRINCIPLES. PRELIMINARY TESTS

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INTRODUCTION AND THEORY

The XRF analysis of powders in the form of thin films has been known for many years. Salmon (1962) summarized the theory and applied the thinfilm method to analysis of mineral samples. Salmon's approach was to encapsulate the powdered sample between sheets of mylar and present it upside down to the X-ray beam in a spectrometer using inverted geometry. He experienced difficulties in preparation of uniform samples and in attenuation of the X-ray beam by the mylar film.

During the last 30 years the method has been used very little, but we have found that the use of modern closely coupled X-ray tube-sample geometries, upright sample positioning and the elimination of the mylar film between the X-ray tube and the sample make the thin film method attractive for environmental Pb analysis of mineral powders at action levels greater than 100 ppm.

The advantages of the method are that only small amounts of sample material are required, and that matrix effects are essentially eliminated. The disadvantages are that the countrates require long counting times for good precision and that weighing steps are required.

The absence of matrix effects allows a simplified calculation of results which is based on a linear proportionality between unknown and a single standard. The countrate per concentration per unit weight is the same for both unknown and standard when there are no interferences. Using the determination of Pb as an example,

$$\frac{C_x}{[Pb]_x \cdot w_x} = \frac{C_s}{[Pb]_s \cdot w_s} \quad \text{.....(1)}$$

Where C is a countrate, w is a weight, subscript s is for standard, and subscript x is for unknown. Rearranging Eq. (1) for determination of the unknown, $[Pb]_x$,

$$[Pb]_x = \frac{C_x \cdot w_s}{C_s \cdot w_x} [Pb]_s \quad \text{.....(2)}$$

PROCEDURE

The sample, as a fine powder, is to be mounted on the sticky surface provided by double faced adhesive film previously attached to a mount substrate appropriate to the spectrometer. The mount substrate can be conveniently made by compressing boric acid or microcrystalline cellulose in a die designed for making pressed powder briquets. The prepared mount is first weighed (tare), then the sample powder is applied, then the mounted sample is reweighed and net weight of the sample determined by subtracting the tare. Detailed instructions follow and are based on use of the Rigaku 3064 spectrometer.

Prepare sample substrate. Double faced adhesive film of most any type will work well provided that it contains no interfering elements. The film cutter shown in Figure 1 is designed to cut a 1 inch circle from film attached to a 37 mm disk that rides in the spectrometer's sample changer. Refer to Figure 1 for names of parts.

1. Apply tape
   a. Invert guide with slots up, and place it on a table
   b. Insert labeled disk, label toward table
   c. Apply tape to disk through centering slot
   d. Remove disk tape, and trim tape to edge of disk
   e. Smooth down tape with plastic sheet or teflon rod

2. Cut disk
   a. Place disk on table with tape up
   b. Place guide over disk with slot toward the table
   c. Lower cutter into guide until it rests on tape
   d. Grip disk through finger recesses
   e. Rotate cutter on tape several times back and forth to cut it

3. Remove guide leaving cutter on disk

4. Hold disk plus cutter together and remove waste tape

5. Store disk in a dust free place prior to weighing if the sample is not to be applied immediately.

Mount sample. The sample should be a powder with a grain size as fine as possible, for it is important that the grains fill the available space without overlap and consequent shadowing.

1. Weigh prepared pellet and tape (tare)

2. Apply sample to tape using disk cutter as a guide
   a. Completely cover tape with sample powder by shaking it in disk cutter

b. Use a soft artist's brush to distribute the sample evenly if necessary
c. Pour off excess sample powder and tap the mount upside down to remove what remains.
d. Carefully wipe out inside of disk cutter
e. Press remaining powder into tape with end of clean teflon cylinder guided by the disk cutter

4. Reweigh and subtract tare

TEST OF THE METHOD

The method was tested by using several geochemical standards having a comprehensive range of Pb concentrations. The standards and instrumental conditions used are listed in Table 1.

TABLE 1. Standards and Instrumental Conditions

Samp No.	Agency	Sample type	ppm Pb
FeR-1	CCRMP	Iron Formation	5200
GXR-2	USGS	Soil	690
SY-2	CCRMP	Syenite	85
VS-N	ANRT	Glass	1000

Instrument: Rigaku 3064 Geigerflex WDXRF spectrometer; Kv/Ma: 60/45; Slits: coarse; Crystal: LiF (200); peak: Pb Lβ; Count: 200 sec

Samples were prepared in triplicate following the procedures given above. The data were reduced using Eq. (2) and the standards treated as unknowns. The results were calculated once using VS-N and again using FeR-1. Background was corrected after measuring peak intensity on a blank. The results summarized in Table 2 below should be considered preliminary. The results are graphically displayed in Figures 2 and 3.

Inspection of the last column of Table 2 shows that the precision of the analysis is on the order of 10 percent The average errors of FeR-1, VS-N, GXR-2, and Sy-2 are 11%, 5% 10%, and 8% respectively. Excluding FeR-1,16, accuracy is good for the two higher concentrations, moderate at 690 ppm and poor at 85 ppm. The rogue value shown by sample FeR-1,16 is unexplained at this time, but we suspect inhomogeneity of the sample. Standard VS-N is an artificial glass, and is expected to be more homogeneous in lead than the natural samples. It does, in fact show the best reproducibility.

Columns 3 and 4 of Table 2 show that results calculated by using FeR-1,18 (5200 ppm) are systematically lower than those calculated by using VS-N,1 (1000 ppm). However, this bias is substantially less than the analytical variation among replications.

Figure 3 shows that calculated and reported Pb concentrations in the standards used for this preliminary study correspond closely. Figure 2 shows that the variation in net countrate per milligram of sample versus reported Pb concentration is substantially linear over a range of three orders of magnitude. This will allow samples as diverse as soils, paint, and household dust to be analyzed with a single well characterized standard.

As presently developed, the method is applicable to environmental "action level" evaluation of total Pb in finely divided materials. The method is simple in that it demands no matrix corrections. In this sense, it is exceptionally direct and free of the assumptions ordinarily found in XRF analyses. It does require careful weighing of small amounts of sample and attention to analytical procedure. We think that its most practical use will be in the analysis of dust collected from selected locations in dwellings.

TABLE 2. Analysis of Pb using FeR-1 and VS-N.

Sampl #	ppm rptd	calc/VS	calc/FeR	cps unk	mg unk	cps/mg
FeR-1,18	5200	5352	5200	1557	184	8.46
FeR-1,16	5200	4216	4096	1020	153	6.67
FeR-1,11	5200	5669	5508	1470	164	8.96
VS-N,1	1000	1000	971	166	105	1.58
VS-N,4	1000	929	902	141	96	1.47
VS-N,6	1000	1077	1046	189	111	1.70
GXR-2,3	690	524	509	63	76	0.83
GXR-2.10	690	474	460	33	44	0.75
GXR-2,14	690	608	591	77	80	0.96
Sy-2,2	85	159	155	23	91	0.25
SY-2,12	85	181	176	29	101	0.29
SY-2,7	85	196	191	33	106	0.31
blank 3				-100		
blank 1				13		
blank 2				1		

REFERENCES

Salmon, Merlyn L. (1962) A simple multielement-calibration system for analysis of minor and major elements in minerals by fluorescent X-ray spectrography. Advances in X-ray Analysis, Wm. M. Mueller, editor, Plenum Press, vol 5., pp 389-404.

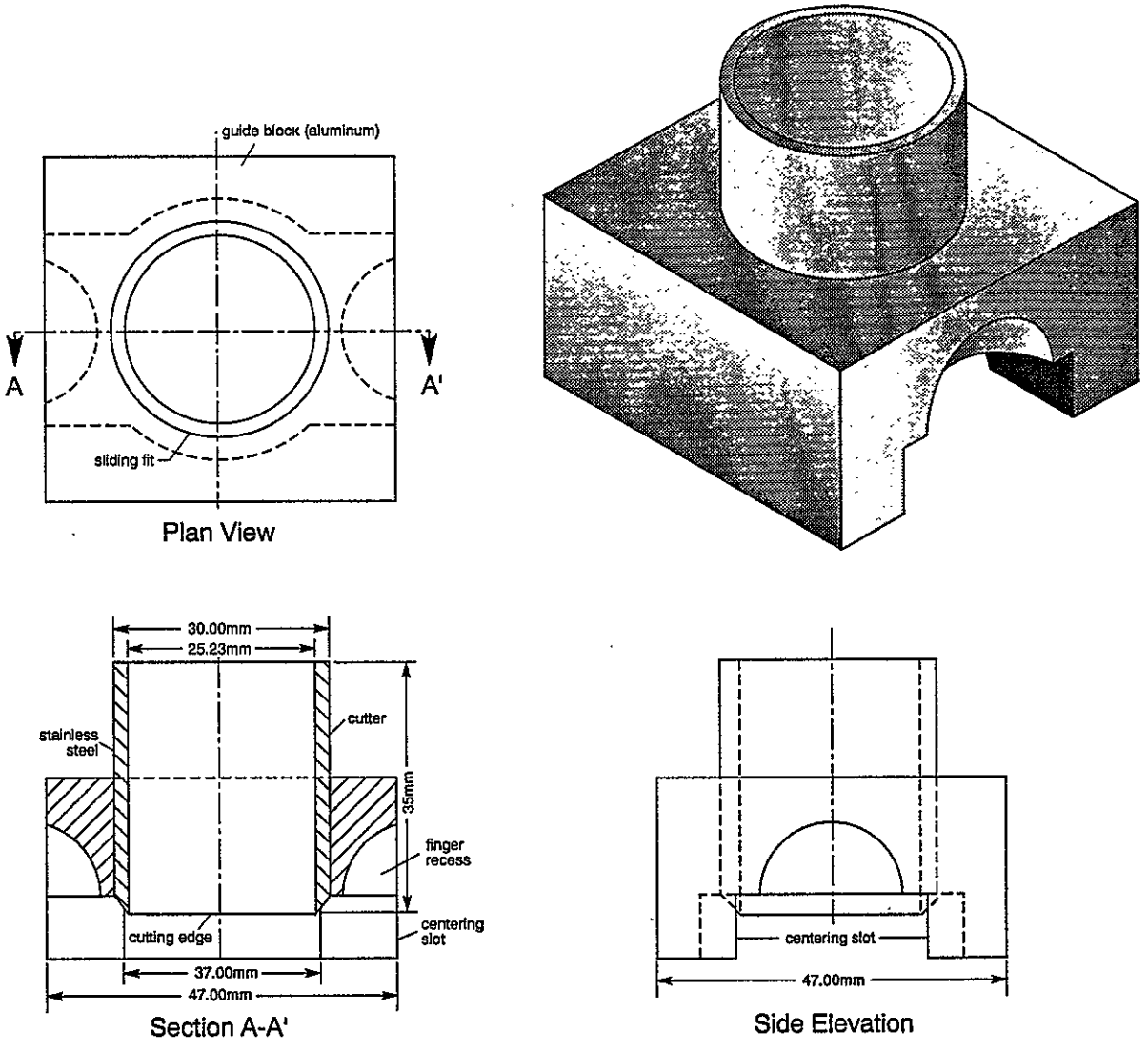

Figure 1. XRF/XRD Tape Cutter

Figure 2. Cps/mg vs. Pb concentration in standards

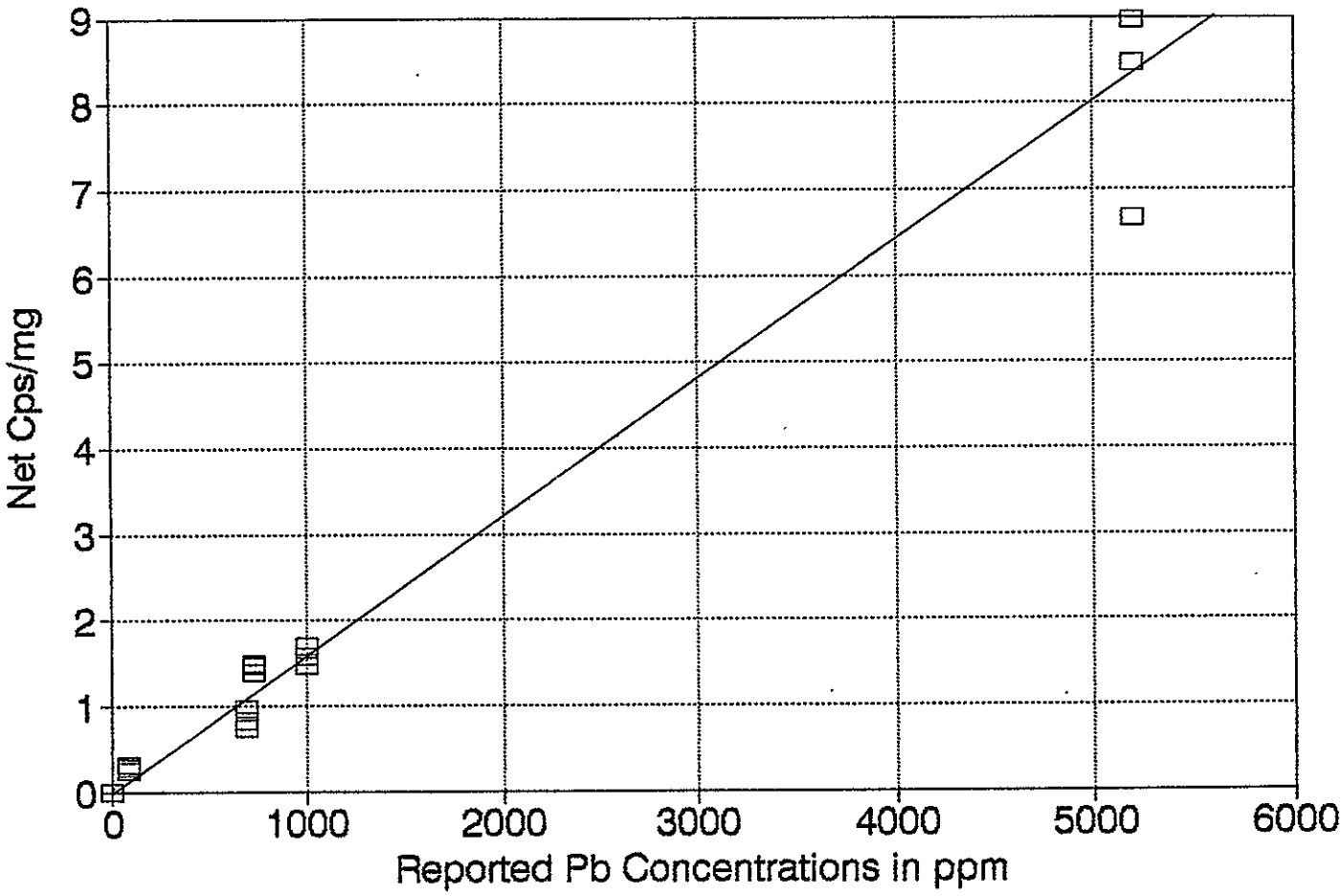

Figure 3. Calculated vs. reported Pb concentration using standard VS-N,1