Analysis of Grass Samples for Lead Content by X-Ray Fluorescence

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X-ray fluorescence is a well known technique for fast, non-destructive, multielement, qualitative analysis. More recently this technique is being used in quantitative work. Its virtues in such applications make it a very useful analytical tool. This paper describes a technique in which X-ray fluorescence can be calibrated with atomic absorption spectrometry and thereby quantified. Specifically, it deals with lead concentrations in grass samples along interstate highways. The report emphasizes the technique that has been developed. Data which have been acquired are not exhaustive but show the potential inherent in the procedure.

Procedure

Grass samples were collected from along I-69 between Upland and Fort Wayne and from I-294 near Chicago. These samples were prepared in two ways: the "cup" method, and the "planchet" method. The cup method is the simpler and quicker procedure. It involves cutting the grass into lengths from 1-2 cm. After drying the sample in a desiccator 1.50 grams are weighed into a Dixie medicine cup. The 30 ml cup is covered with a piece of thin mylar plastic and the sample is ready for counting with the X-ray fluorescence spectrometer.

The planchet method entails more work and a correspondingly longer preparation time. It involves freeze-drying the grass with liquid nitrogen. The grass is cut into 1 cm. lengths. It is placed in a mortar and liquid nitrogen is applied. Upon freezing, the grass can be ground with a pestle and placed in an oven to dry. A constant weight can then be placed in small planchets. The planchet is also sealed with mylar film and the sample is ready to be counted. The advantage of using thin mylar film is that it causes very little attenuation of the X-rays thus allowing for better counting efficiencies.

In both methods of preparation the samples were counted for 80 minutes with a 400 channel analyzer. A blank which contained no grass was also prepared and counted in the same manner as the samples.

After counting, both the lead alpha and lead beta peaks were integrated for each sample. The background count of the blank was also integrated and subtracted from the peak integral thus giving a net peak integral for each sample. Table 1 shows the results obtained by both methods and lists the corresponding lead concentration in parts per million.

In order to quantify the X-ray fluorescence technique a calibration was made using atomic absorption spectrometry (A.A.). Each sample of grass was also analyzed for lead content with A.A. The grass was cut into small pieces and 0.300 grams were weighed and placed in a

TABLE 1. *Lead concentration in grass samples prepared by the cup and planchet methods.*

	Cup Method		Planchet Method		
Sample Number	Alpha Peak Integral	Beta Peak Integral	Alpha Peak Integral	Beta Peak Integral	Lead Concentration (ppm)
2	3161	3039	791	704	333
5	1914	1961	- - -	- - -	150
6	2637	2593	452	396	167
11	4205	4309	986	865	433
13	8122	8430	2203	2085	1100

beaker. Ten ml. of concentrated nitric acid was added and the grass was digested for 24 hours. It was assumed here that all the lead in the sample went into solution as lead nitrate even though some fibrous grass material did not dissolve. The organic residue is filtered out and the filtrate is diluted to 100 ml. It is essential to dilute the dissolved samples so that the lead concentration does not exceed the spectrometer's linear working range for lead which is up to 20 ppm.

Lead standard solutions are prepared using the methods described in "Standard Conditions for Lead" (1). The A.A. spectrometer is first calibrated with these standard solutions and then the samples are analyzed. The lead concentrations can then be expressed as parts of lead per million parts of grass. These concentrations are shown in Table 1 for five typical samples.

Results

A graph can now be plotted of net peak integral counts (obtained by X-ray fluorescence) versus lead concentration in ppm (obtained with the A.A. spectrometer). This was done for the data collected with each of the two X-ray methods. The cup method yielded considerable variation between results based on the alpha and the beta peak integrals. There appeared to be no general pattern, and the variation can most probably be attributed to matrix inconsistencies from one sample to another. Figure 1 presents the graphical data obtained by the cup method. In the planchet method the peak integrals were much more consistent with the alpha peak integrals always being greater than the betas. Parallel straight lines can be drawn through the data points for both the alpha and the beta integrals as shown in Figure 2. This confirms that a much more consistent sample was obtained in the planchet method which relies on the freeze-drying technique.

Conclusions

X-ray fluorescence can be used quantitatively for the analysis of heavy metals in grass samples and in other vegetation if the instrument is calibrated with another method such as atomic absorption spectrometry. Once calibration curves are plotted, one has a quick and effective method of quantitative determination. If speed is a major consideration the cup method may be useful since it allows for rapid sample preparation. The lead concentration cannot be determined as accurately, but
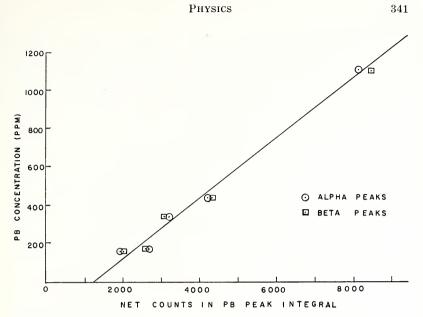
FIGURE 1. *Lead concentration in grass samples. Data obtained by X-ray fluorescence using the cup method.*
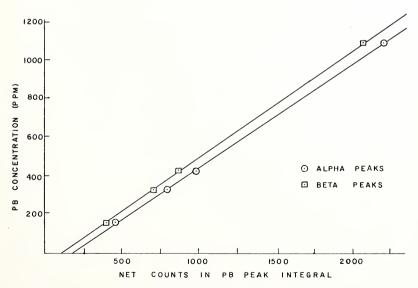

FIGURE 2. *Lead concentration in grass samples. Data obtained by X-ray fluorescence using the planchet method.*

a general range of concentrations can be obtained, which in many analyses is sufficient. If more accuracy is desired the planchet method, which utilizes freeze-drying, can be used with either the alpha or beta integral peak plot, or both peaks can be used as a check of results. Sample preparation is slightly more involved, but results are greatly improved. Both methods, however, are much quicker than other routine analytical chemistry techniques.

Literature Cited

Standard Conditions for Lead. 1973. Analytical Methods for Atomic Absorption Spectrophotometry. Perkin-Elmer Corporation, Norwalk, Connecticut.