

Working Paper 333

THE EFFICIENCY OF DIFFERENT METHODS
OF EXTRACTING LEAD FROM STREET DUST

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ABSTRACT

Several techniques for the analysis of lead in street dust have been reported in the literature. The results presented here are an attempt to determine the influence of analytical technique on the reported lead levels. The results indicate that mean lead level is depressed by sample grinding, and by increases in ashing temperature. Higher lead levels are produced by refluxing in comparison to simple boiling. When four techniques were separately evaluated differences of between 250 and 450 ppm were found which could be ascribed solely to differences in technique.

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Introduction

There is no standard method for extracting lead from environmental materials such as street dust. This has had the result that each survey of the lead content of street dust has used a different analytical method; thus making comparisons of the Pb levels in different cities difficult. A series of experiments was carried out to determine the differences in extraction efficiency of four methods reported in the literature concerning city wide lead surveys in Britain. These are:

- (i) Day, J.P. *et al.* (1975) Lead in urban street dust, *Nature*, 35, pp. 343-5. This examined Pb levels in Manchester. Samples were dried at 120°C and homogenised by grinding. 1g was boiled with 2M HNO₃ for 30 minutes. Pb content was determined by atomic absorption spectrophotometry (AA).
- (ii) Archer, A. and Barratt, R.S. (1976) Lead levels in Birmingham dust, *Science of the Total Environment*, 6, pp. 275-86. Samples were dried at 100°C and sieved (20 mesh BS nylon sieve) before ashing in silica at 550°C for 30 minutes. 1g of the ashed sample was refluxed for 15 minutes with 25% (v/v) HNO₃. The cooled solution was diluted to 50 or 100 mls, filtered, and analysed by AA.
- (iii) Farmer, J.G. and Lyon, T.D.B. (1977) Lead in Glasgow street dirt and soil, *Science of the Total Environment*, 8, pp. 89-93. Samples were dried and ground. 1g was then leached overnight at 60°C with 100 ml 25% CH₃CO₂H / 0.25M NH₄OH.HCl. This was then centrifuged and the supernatant liquid evaporated to dryness. The residue was dissolved in 100 ml 1M HCl and analysed by AA.
- (iv) Duggan, M.J. and Williams, S. (1977) Lead in dust in city streets, *Science of the Total Environment*, 7, pp. 91-7. This examined Pb levels in London. Samples were sieved through a 30 mesh BS (500µm) stainless steel sieve, followed by wet-extraction with hot aqua-regia*. Analysis by AA.

*Aqua-regia is a mixture of 1 part HNO₃ and 3 parts HCl.

The method reported by Duggan and Williams (Method iv) was, however, insufficiently detailed and precise to enable the experiment to be replicated. The details omitted were: the weight of dust sample, the volume of aqua-regia, the length of time of the extraction, and whether the samples were boiled or refluxed. This method was therefore excluded from this series of experiments. Since the work of the present author was sited in Leeds metropolitan area, the method used by the Leeds Public Analyst in examining Pb levels in street dust for Leeds City Council Environmental Health Department was also examined.

(v) Leeds Public Analyst

Samples were dried at 100°C and sieved through 0.5 mm (30 mesh BS) stainless steel sieve. 1g of the sieved sample was ashed for 30 minutes at 350°C, and then refluxed for 15 minutes with 25 mls of 25% HNO₃. The solution was cooled, filtered and diluted to 100 mls and analysed by AA.

Method

To identify variation caused by analytical technique four experiments were conducted to determine the effect of grinding, ashing, boiling and refluxing. In addition, each reported analytical technique was evaluated separately.

A single large sample of street dust was collected on which to test the different methods of analysis. The dust sample was mixed thoroughly and thus assumed to be fairly uniform and three replicates were completed throughout.

Experiment 1. To determine the effect of grinding the sample

- (a) The sample was dried and sieved through a 0.5 mm stainless steel sieve.
- (b) The sample was dried and ground using a Janke and Kunkel KG 1KA Analytical mill A10. (NB. Neither Day et al. nor Farmer and Lyon gave details of method of grinding).

In both cases 1 g of sample was then ashed for 30 minutes at 350°C. The sample was then refluxed for 15 minutes with 25% HNO₃, and the solution cooled, filtered, diluted to 100 mls and analysed by AA.

Experiment 2. To determine the effect of dry-ashing temperature

In both cases the samples were dried and sieved through a 0.5 mm stainless steel sieve.

- (a) lg was ashed at 350°C for 30 minutes (Leeds Public Analyst)
- (b) lg was ashed at 550°C for 30 minutes (Archer and Barratt)

Then the samples were refluxed for 15 minutes with 25% HNO₃, and the solution cooled, filtered, diluted to 100 mls and analysed by AA.

Experiment 3. To determine the differences between boiling and refluxing

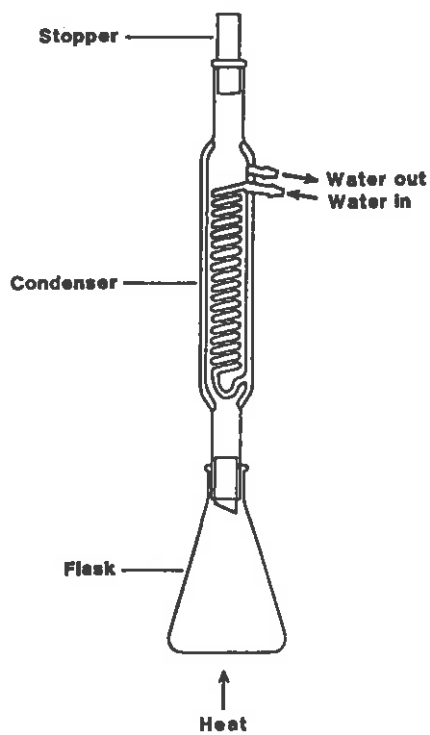
In all cases the samples were dried and sieved through a 0.5 mm stainless steel sieve. Then lg of the sieved sample was ashed for 30 minutes at 350°C.

- (a) The sample was boiled in an open beaker for 15 minutes with 25% HNO₃.
- (b) The sample was boiled in an open beaker for 30 minutes with 25% HNO₃.
- (c) The sample was 'refluxed' in a beaker with a watchglass placed over the top (to reduce evaporative losses) for 15 minutes with 25% HNO₃.
- (d) The sample was refluxed (see Figure 1) for 15 minutes with 25% HNO₃.

Experiment 4. To determine the differences between analytical methods reported in the literature

- (a) The sample was analysed by method (i), Day et al.
- (b) The sample was analysed by method (ii), Archer and Barratt
- (c) The sample was analysed by method (iii), Farmer and Lyons
- (d) The sample was analysed by method (v), Leeds Public Analyst.

Fig. 1 : Apparatus for refluxing



Results

The results of the four experiments specified above are given in Tables 1 to 4 respectively.

Discussion

The results presented in Table 1 indicate that the ground samples gave lower Pb values than the sieved samples. This may be explained by the nature of the samples being examined. Firstly, most of the Pb in street dust is concentrated in the small particle range, and secondly, these small particles may form a coating round the larger particles. Grinding will therefore break up these large particles to produce a homogeneous material which will facilitate sub-sampling, and expose a larger surface area to the action of the reagents used in the analysis. However, the analytical chemists' ideals may be considered inappropriate when dealing with environmental samples, as it is the exterior coating of the particles which are of interest and not the constituents of the core. In addition the grinding process inevitably leads to the loss of some of the sample in the form of dust, which will cause an alteration in sample composition.

Table 2 demonstrates the effect of varying the dry-ashing temperature on the extraction of Pb. Samples are ashed in order to decompose any organic matter, as carbonaceous material will be oxidised to CO_2 . Analysis of the non-volatile components follows solution of the residual solid. The recommended maximum dry-ashing temperature for the analysis of Pb is 700°C (Whiteside, 1979), and the results of table 2 may indicate that there are increased losses of Pb as the ashing temperature is increased towards this maximum. Unfortunately the technique of dry-ashing has disadvantages. Skoog and West (1976) suggest some losses of heavy metals result from the mechanical entrainment of finely divided particulate matter in the convection currents around the crucible. Secondly, volatile metallic compounds may be formed during the ignition. And thirdly, the complete recovery into solution of the supposedly non-volatile elements is uncertain. Hence although dry-ashing is the simplest of all methods for decomposing organic matter, it is often the least reliable.

Table 1. The effect of grinding

Sample Treatment	\bar{x} Pb value ppm	Average Deviation from \bar{x}	Relative Deviation from \bar{x}	Range ppm	Standard Deviation	Coefficient of variation
Sample sieved	1783	142	8%	340	186	10%
Sample ground	1517	62	4%	150	82	5%

Table 2. The effect of ashing temperature

Sample Treatment	\bar{x} Pb value ppm	Average Deviation from \bar{x}	Relative Deviation from \bar{x}	Range ppm	Standard Deviation	Coefficient of variation
Sample ashed at 350°C	1783	142	8%	340	186	10%
Sample ashed at 550°C	1523	136	6%	240	123	8%

Table 3. Comparisons of boiled and refluxed samples

Sample Treatment	\bar{x} Pb value ppm	Average Deviation from \bar{x}	Relative Deviation from \bar{x}	Range ppm	Standard Deviation	Coefficient of variation
Sample boiled 15 mins	1607	136	8%	360	185	12%
Sample boiled 30 mins	1577	58	4%	140	76	5%
Sample 'refluxed' in beaker with watchglass	1480	87	6%	250	125	9%
Sample refluxed 15 mins	1783	142	8%	340	186	10%

Table 4. The differences in analytical techniques

Sample Treatment	\bar{x} Pb value ppm	Average Deviation from \bar{x}	Relative Deviation from \bar{x}	Range ppm	Standard Deviation	Coefficient of variation
Day et al.	1453	31	2%	80	42	3%
Archer and Barrett	1523	91	6%	240	123	8%
Farmer and Lyon	1316	15	1%	40	21	2%
Leeds Public Analyst	1783	142	8%	340	186	10%

Table 3 shows that the samples which were refluxed gave the highest Pb values. The samples boiled in an open beaker resulted in a decreased Pb recovery of 175 ppm, which may be due to evaporative losses. Similarly an increased boiling time led to further losses of Pb. The samples 'refluxed' in a beaker with watchglass also showed losses of Pb, contrary to expectations, which cannot be explained by the author.

Table 4 compares the extraction efficiency of the four analytical methods. This indicates that differences attributable to the method of analysis may vary from 250-450 ppm. The lower levels of Pb recovery may be explained by the different sample treatment (experiments 1-3) and/or different extractant solutions. There are two important points to note. Firstly, with reference to Figure 2 it is evident that greater efficiency in extracting Pb is gained at the expense of precision. Thus whilst the method used by the Leeds Analyst recovered the highest \bar{x} Pb levels (\bar{x} 1783 ppm) the coefficient of variation was 10%; whereas Farmer and Lyon's method yielded the lowest \bar{x} Pb levels (\bar{x} 1316 ppm), but a coefficient of variation of only 2%. Secondly, methods (i) and (iii) which ground the sample achieved better precision, coefficients of variation of 3% and 2% respectively, presumably through achieving a more homogeneous sample. In order to test whether the coefficient of variation found in method (v) was a chance result of variations in a large original dust sample (approx 100g), the results of previous replicate analyses were studied. These indicated that replicates on small dust samples (approx 5g) analysed by this method also yielded coefficients of variation of 10%.

A series of t-tests was used in order to evaluate whether the differences in \bar{x} Pb value obtained by the different analytical methods were significant. Table 5 shows the results of the t-tests at a rejection level of 5% ($\alpha = 0.05$).

Fig. 2 : Graphical representation of mean and standard deviation values from experiment 4

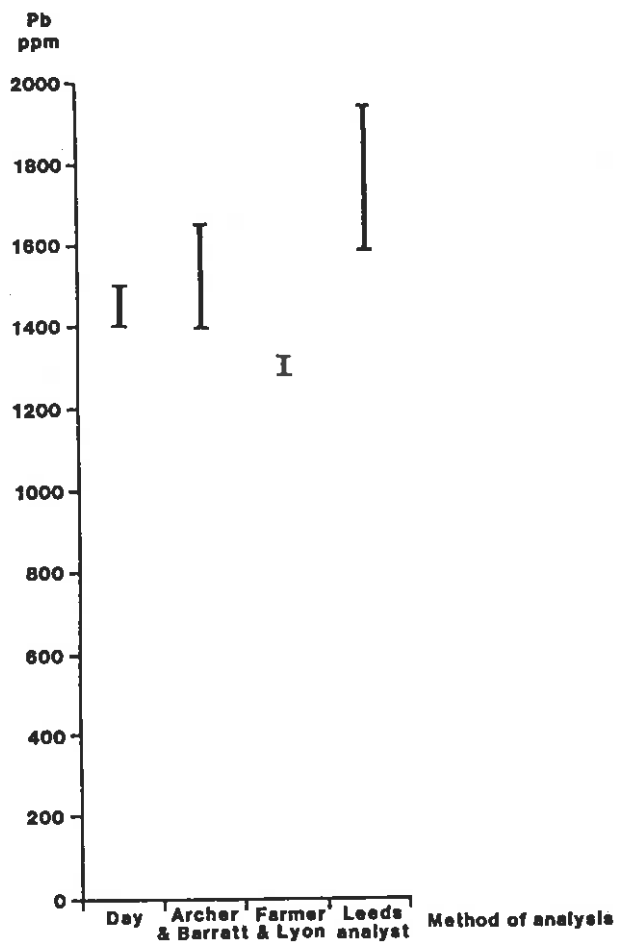


Table 5.

	Day	Archer and Barratt	Farmer and Lyon	Leeds Public Analyst
Day	-	X	✓	✓
Archer and Barratt	X	-	X	X
Farmer and Lyon	✓	X	-	✓
Leeds Public Analyst	✓	X	✓	-

X = No significant difference

✓ = significant difference

Hence there are significant differences between results obtained by the Leeds Analyst's method and the methods of Day et al. and Farmer and Lyon but no significant difference between the Leeds Analyst's and Archer and Barratt's results.

Table 6 gives the actual \bar{x} Pb levels of different cities as reported by various authors.

Table 6.

City	Method of Analysis	\bar{x} Pb value	Estimated "Corrected" value
Manchester	Day, et al.	970 ppm	1145
Birmingham	Archer and Barratt	932 ppm	-
Glasgow	Farmer and Lyon	960 ppm	1210
Leeds	Present author *	566 ppm	-

*Results determined using the technique ascribed to the Leeds Public Analyst (see above).

The experimental evidence suggests that the \bar{x} Pb values for Manchester and Glasgow may be underestimated when compared to the data for Leeds. From experiment 4 it is thought that differences in analytical methods may account for differences of 18% and 26% respectively, ie. approximately 200 ppm, and these estimated 'corrected' values are entered in column 4 of Table 6.

Conclusion

Considerable caution must be exercised when comparing Pb levels in street dust in one city to another. Differences in the analytical method used in extracting the Pb may account wholly or partially for the different \bar{x} Pb values. These problems will persist until there is agreement on a standard method of Pb extraction from street dust.

Bibliography

1. Day, et al. (1975) Lead in urban street dust, *Nature*, 35, 343-5.
2. Archer, A. and Barrett, R.S. (1976) Lead levels in Birmingham dust, *Sci Total Env*, 6, 275-86.
3. Farmer, J.G. and Lyon, T.D.B. (1977) Lead in Glasgow street dirt and soil, *Sci Total Env*, 8, 89-93.
4. Duggan, M.J. and Williams, S. (1977) Lead in dust in city streets, *Sci Total Env*, 7, 91-7.
5. Whiteside, P.J. (1979) *Pys Unioam AA Data Book*.
6. Skoog, D.A. and West, D.M. (1976) *Fundamentals of analytical chemistry*, 3rd edn., Holt, Rinehart and Winston, New York.

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