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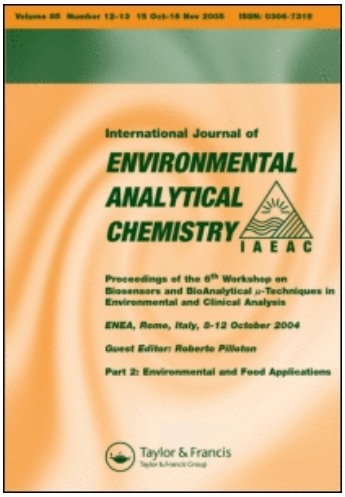

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Quantitative Intermethod Comparison of Energy Dispersive X-ray Fluorescence and Atomic Absorption Spectrometry for the Analysis of Urban Dusts and Fly Ash†

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If environmental analytical chemistry is to be practiced on a routine scale involving a great number of laboratories, certain measures have to be taken to insure the comparability of data; one of these measures is the verification of the results with known materials.

In the course of the development of known materials a detailed intermethod comparison of energy dispersive X-ray fluorescence and atomic absorption spectrometry of urban dust samples from three different cities was performed.

The agreement of results is satisfactory as the discrepancies between the values produced by the two methods are generally below 10% of the content.

Some performance characteristics of the two methods are compared. The experiments were designed to give error estimates for the most likely sources of error including the instrumental error of repetitive measurements (AAS and EDXRF), the decomposition (AAS) and fusing (EDXRF) error, the calibration error (AAS) and the error of the bag-house sampling procedure (EDXRF). It is shown that with a live time of 1000 s the instrument precision of EDXRF is generally better than that of AAS and that the bag-house sampling procedure calls for careful blending of the dust before proceeding with the specification of elemental contents.

The analytical results are verified with Fly Ash, SRM 1633, from the National Bureau of Standards.

KEY WORDS: dust analysis, intermethod comparison, energy dispersive X-ray fluorescence, atomic absorption spectrometry, experimental design.

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†Dedicated to a.o. Univ.-Prof. Dipl. Ing. Dr. techn. W. Limontschew on the occasion of his 60th birthday

INTRODUCTION

As analytical results are frequently the basis for legal action the detection of systematic errors is an important goal for everybody working in the field of environmental analytical chemistry.

Three major devices are commonly used to test an analytical procedure:[1] measurement of known materials, comparison with other measurement procedures and comparison with modifications of a given procedure.

The general aim of this work is directed toward the development of "known materials" with respect to the quantitative elemental composition of environmental dust samples; to this end a known material resembling the matrix of the dusts as close as possible, Fly Ash SRM 1633 issued by the National Bureau of Standards,[2] was used to test two independent methods of analysis, the energy dispersive X-ray fluorescence (EDXRF) and the atomic absorption spectrometry (AAS) with flame and electrothermal atomization. As the experimental details of this work are extensively described elsewhere[3-7] this paper is primarily devoted to the identification of error components relevant to each of the two methods; carefully planned experiments were evaluated to estimate the relative size of errors either involved in the different steps of analysis or attributable to the inhomogeneity of the dust samples. In addition to this it was tried to compile and compare some performance characteristics[8-11] to give a more realistic picture of the overall merits of the two methods for the analysis of urban dusts.

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EXPERIMENTAL

The instruments used in this study are briefly described in Table I and as they are standard equipment, commercially available, no further description is necessary. The elements determined by the two methods are given in Tables II and III. The dusts under investigation are listed in Table IV; in addition to the Standard Reference Material 1633 Fly Ash, settled particulate matter from two origins (Graz and Vienna) and airborne particulate matter from St. Louis, Missouri, are analysed. The sampling of the U.S. dust was accomplished under the direction of the National Bureau of Standards, Washington D.C.

The standards for the AAS analyses are prepared according to the Perkin-Elmer Handbook,[12] the experimental conditions are optimized with respect to the burner position and fuel/oxidant ratio or the temperature program respectively. Less sensitive lines are utilized whenever dilution can be avoided by doing this. For the electrothermal atomization argon is used at a flow rate of 1.5 l/min. The D_2-lamp has not been used

TABLE I

Comparison of general features of AAS and EDXRF

Instrument	AAS	EDXRF
Type	Perkin Elmer 403 with HGA 72	Kevex 4600 Northern Multi-Channel Analyzer (II Series) and General Electric power supply
Excitation	hollow cathode lamps	Tungsten X-ray tube with automatic dial a secondary target arrangement
Mode	single element	multielement
Dynamic range	10^2	10^4–10^5
Theory	not fully developed	processes are well understood
Cost of instrumentation	appr. $50000	appr. $150000
Data reduction	simple	complex

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TABLE II

Elements determined with AAS

	Flame		
Atomization	C_2H_2/air		C_2H_2/N_2O
Elements	Zn, Mn	Fe	Pb, Cu, Cr

TABLE III

Elements determined with EDXRF

Target	Nickel	Molybdenum
Heavy absorber	WO_3	La_2O_3
Elements	Ca, Ti, V, Cr, Mn, Fe	Fe, Ni, Cu, Zn, Pb, Sr

for compensation of unspecified signals. An individual test for interferences is applied for each element separately; this newly developed procedure[13] is based on the sequential comparison of the slopes of the standard and sample solution. In this test the great discriminating power of sequential tests is utilized to compare the sensitivities of the determination of the analyte in the standard and in the decomposition solution. For this kind of test it can be shown that the experimental work is reduced according to the absolute size of the difference between the two sensitivities and, thus,

TABLE IV

Characteristics of the dusts used in the analyses

Origin	Type	Sampling method	Fractionating method	Particle size
Graz, Austria	settled street dust	sweeping	sieving	$<50\,\mu m$
Vienna, Austria	settled street dust	sweeping	sieving	$<50\,\mu m$
St. Louis, Missouri, U.S.A.	airborne particulate matter	air bag sampling	none	not determined
Electric power plants	coal fly ash SRM 1633	electrostatic and mechanical collectors	sieving	$<88\,\mu m$

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the experimental effort can be kept at a minimum. A similar efficiency of the usually applied statistical tests where the number of experiments has to be determined before running the test cannot be expected. The quantitation is performed employing peak height evaluation in case of electrothermal atomization and digital absorbance readings in case of flame atomization.

40–50 $\pm$ 0.2 mg dust sampled are placed in a closed PTFE-vessel after drying the dust at 110°C overnight; 2 $\pm$ 0.02 ml HNO_3 65% and 2 $\pm$ 0.02 ml HF 40% (suprapur) are added and the mixture is dissolved at 160 $\pm$ 10°C for 3 hours under pressure; after cooling the solution is transferred to a 100 ml beaker containing approximately 30 ml saturated H_3BO_3 solution (80 $\pm$ 10°C) in distilled water and it is kept below boiling point for about half an hour; after cooling the sample solution is transferred to a 50 ml graduated flask and made up to volume with distilled water. This procedure is virtually equivalent to the one suggested in Refs. 14–17.

To calibrate the EDXRF system, synthetical $Li_2B_4O_7$ glass beads are prepared, using the well-known "fusion and direct solidification-technique".[18] Known amounts of elements (organometallic compounds, oxides or nitrates) are mixed with Fe_2O_3, $CaCO_3$ and SiO_2 to give a total weight of 0.5 $\pm$ 0.1 g. Quantitation is achieved employing K_α- and L_α-peak area evaluation, setting peak energy windows equal to the full widths at half maximum. For Pb the L_β-peak area was occasionally evaluated, as well.

Monoenergetic, secondary excitation of the specimens is carried out with a Ni-target (in vacuum) and a Mo-target/Mo filter arrangement. Primary excitation of the secondary targets is done by a tungsten tube

using 45 KV/60 mA for the Mo and 25 KV/30 mA for the Ni arrangement. To obtain reasonable count rates, live time was set on 1000 s, employing an automatic sample changer and write out on punched tape. For element concentrations below 0.1% the linear least square fit calibration method was adequate, for higher element concentrations treatment of interelement effects is necessary.[19] Spectral interferences, peak overlaps and background are corrected for by empirical methods.[20]

Sample preparation is done by fusing 0.25 g to 1.0 ± 0.0002 g dust with 6 ± 0.1 g $Li_2B_4O_7$ and 0.5 ± 0.01 g of heavy absorber (La_2O_3 or WO_3) using special non-wetting 95% Pt/5% Au alloy crucibles and the automatic fusion device PUFF (Ångstrom Inc.). By addition of 4 ± 0.1 g NH_4NO_3 to the flux preashing or digesting the sample before fusion becomes unnecessary. For the investigated dust samples no significant loss of an element during the fusion procedure at 1300°C was observed, with the exception for bromine compounds which are partially expelled from the sample.

Prior to analysis, the surface of the borax beads is ground with a diamond disk and polished with a 400 grit silicon carbide abrasive disk.

If not specified differently, all reagents used are of p.a. grade.

The data reduction for the EDXRF-results is performed by using a Univac 1108, but can also be handled by a smaller computer. The analysis of nested designs and the data reduction for the AAS-results are accomplished with a HP-97 Programmable Calculator from Hewlett-Packard. The program for the evaluation of the experimental design is available upon request.

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DESIGN OF EXPERIMENTS

Trained manpower and sophisticated laboratory equipment can be used effectively only, if the experiments are carefully designed.[21] Due to the different processes underlying the two analytical methods under investigation, different sources of error need to be taken into account for the two procedures.

For the AAS measurements two sources of error other than the instrument error were considered: one was attributable to the long-term error (one to two months) and to the inhomogeneity of the material and was tested for by making separate dissolutions of 50 mg portions of the dusts; the other one could be related to short time variations (two to three days) and was mainly identified as stemming from separate calibrations and readjustments of the instrument. The third component was the one associated with replicate determinations to give an estimate of the basic reproducibility of the instrument. The experiments were arranged in an order which is referred to as "nested design" and extensively described

in literature.[22,23] Nested designs where the components of variations are determined at different steps in an analytical procedure are apt to identify effectively specific sources of random errors occurring in the course of an analysis. This information is not available if the random errors are pooled to give an overall estimate as is generally reported for analytical procedures. To identify a single step as cause of the major portion of the overall random error can help greatly in further developing the method since this step has to be improved to assure a reduction of the random error of the entire analytical procedure. A priori, it was not expected that all dusts exhibit the same reproducibility of results; thus, the different dust samples were not entered in the same design. This had the additional advantage of giving a constant variance over all classes, which is one of the necessary assumptions in an analysis such as this.[23] The degrees of freedom were not less than 12 on the lowest stage (residual error) and not less than 2 on the highest stage (long time drift, inhomogeneity of dusts).

For the EDXRF experiments three different questions had to be elucidated in this work:

- How big is the influence of differing sample portions upon the systematic and random errors of the results?
- Is there any between-pellets inhomogeneity detectable for some or all elements?
- Did the bag-house sampling procedure for the St. Louis dust yield any additional variation of results with respect to the different sections within one bag-house?

No provisions were made in the experimental design for between calibrations variance, since the instrument was recalibrated for every run (16 samples per run) with one of the standards used in the original calibration. For this purpose the standard with the highest counting rate was taken to ensure sufficient counting statistics. The long-time stability of the glass bead standards permits this shortcut in calibration with virtually no sacrifice of accuracy.

To study the quality of results in dependence on the amount of dust sample per glass bead, four glass beads with 0.25, 0.5, 0.75 and 1.0 g Fly Ash were prepared and measured three times. A two stage nested design was chosen to deal with the problem of between-pellets inhomogeneity. This was done for Cu, Ni, Zn, Pb and Fe for all three urban dusts, and for all elements listed in Table III for the St. Louis dust. Three pellets were prepared identically for this purpose.

The third question was related to the within bag-house sampling variance of the St. Louis dust. This problem was approached by using the same design as explained in the last paragraph for the between-pellets

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inhomogeneity and adding to this a third level of nesting: dust from three different sections of one bag-house made up this third level plus a sample of the "left-over" dust not deposited directly in the bags, but in the space between them. From each of these four zones three pellets were molten and analysed.

The scheme of interpretation of data can again be taken from literature.[22,23]

RESULTS AND DISCUSSION

Comparison of results

A comparison of analytical results obtained with AAS and EDXRF is

TABLE V

Comparison of results for some elements.
All data are given in % wt/wt

Element	Method	Graz	Wien	St. Louis	Fly ash
Ca	EDXRF	12.5	15.2	6.1	4.6
	OTHER[24]	—	—	—	4.7
Ti	EDXRF	0.560	0.300	0.439	0.75
	OTHER[24]	—	—	—	0.74
V	EDXRF	0.024	0.019	0.032	0.0216
	OTHER[2]	—	—	—	0.0214
Cr	EDXRF	0.0141	0.0061	0.0416	0.0131
	AAS	0.0133	0.0071	0.0427	0.0135
	OTHER[2]	—	—	—	0.0131
Mn	EDXRF	0.130	0.045	0.065	0.050
	AAS	0.124	0.047	0.062	0.044
	OTHER[2]	—	—	—	0.0493
Fe	EDXRF[a]	4.1	2.3	4.2	6.2
	AAS	3.9	2.2	4.0	5.8
	OTHER[24]	—	—	—	6.2
Ni	EDXRF	0.0038	0.0028	0.0074	0.0093
	OTHER[2]	—	—	—	0.0098
Cu	EDXRF	0.029	0.009	0.045	0.0123
	AAS	0.033	0.011	0.042	0.0129
	OTHER[2]	—	—	—	0.0128
Zn	EDXRF	0.081	0.054	0.328	0.0200
	AAS	0.081	0.052	0.317	0.0234
	OTHER[2]	—	—	—	0.0210
Pb	EDXRF	0.045	0.095	0.444	0.0065
	AAS	0.046	0.110	0.446	0.0081
	OTHER[2]	—	—	—	0.0070
Sr	EDXRF	0.022	0.027	0.016	0.126
	OTHER[24]	—	—	—	0.170

[a]The EXDRF determination of Fe was done with La_2O_3 as heavy absorber and with Ni as secondary target.

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given in Table V. Just very few of them differ by more than 10%, among them are the results for Pb in the dust from Vienna and in Fly Ash. It will be shown that material inhomogeneities are the probable cause for this finding. No estimate of the reproducibility of data is made in Table V since these estimates are discussed in more detail later on. Where certified[2] values are not available, the results published by Ondov *et al.*[24] are given for the SRM Fly Ash. This paper[24] was chosen because it represents the most complete study available. In general, the agreement is satisfactory.

Error components in AAS

For the determination of the influence of various sources of error upon the results of AAS analyses it was found that a considerable random error has to be expected for most elements; estimates of these errors are given in Table VI. The reason for this is certainly the limited dynamic range of absorbance measurements and the occasionally high noise of hollow cathode lamps. To improve this situation other light sources, such as

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TABLE VI

Estimate of error components for the AAS analyses

Element	Estimate of error due to	Graz	Vienna	St. Louis	Fly ash
	decomposition	19	19^{xx}	28^{x}	—
Cr	calibration	19^{x}	—	17	14^{x}
	instrument	7	8	23	11
	decomposition	38	82^{xx}	61^{x}	38^{x}
Mn	calibration	41^{xx}	16	46^{xx}	21^{xx}
	instrument	23	20	26	14
	decomposition	2600^{xx}	2260	2750^{xx}	3300^{x}
Fe	calibration	—	1200^{x}	750	1300^{xx}
	instrument	860	630	740	1000
	decomposition	6	8^{xx}	34^{x}	15^{x}
Cu	calibration	—	—	8^{x}	3
	instrument	11	6	14	6
	decomposition	—	38^{x}	520^{xx}	—
Zn	calibration	12	11	—	20^{xx}
	instrument	18	16	140	12
	decomposition	—	—	710^{x}	—
Pb	calibration	26^{xx}	180^{xx}	—	8^{x}
	instrument	19	140	340	10

All values are given in ppm: the confidence level for the error due to decomposition and calibration is 0.1, one x indicates a confidence level of 0.05 and two x's a confidence level of 0.01. When no figure is given, the error is not significant at a confidence level of 0.1.

electrodeless discharge lamps,[25] with a more stable output could be used and the averaging of signals could be done over more than 100 measurements.

Differences between the error components of the same origin but for different dust samples can be attributed to two facts: one, the error components as given in Table VI represent estimates and include appreciable uncertainties; this can be shown by computing confidence limits.[22] And, second, the samples had to be diluted very differently according to the metal content, so that the signal falls within the linear range of the calibration curve. This second aspect is very important and has to be kept in mind when analysing environmental samples with widely varied metal content. The same argument applies to the error component due to calibration. It should be remembered that the experiments were conducted in such a manner that all kinds of short time variations are included in this error component termed "calibration" (see chapter on Experimental Design).

In the course of the development of known materials special consideration has to be given to sample inhomogeneities. Very far reaching assumptions need to be made if a full statistical treatment of this problem is attempted;[26,27] as a consequence practical tests for the homogeneity of the material are routinely performed for standard reference materials.[2] For the decomposition technique employed in the AAS analyses several elements appear to be distributed inhomogeneously, albeit the large errors due to the instrument and to the calibration prohibit a more sensitive detection of the error due to the decomposition. The best homogeneity exhibits the dust sample from Graz; an explanation for this probably is that Graz has the least industry of the cities covered in this study and thus fewer "types" of dust grains with a much narrower range of element concentrations among the dust grains. Apart from Fly Ash which needs a sample of 250 mg to arrive at the certified contents,[2] the St. Louis dust shows the greatest variability between separate decompositions. This may be due to the longer sampling interval (appr. 2 years) as well as to the heavy industry of St. Louis producing very different kinds of dust grains with distinct segregation effects. Another cause of variation might be the sampling procedure; this aspect is discussed in more detail for the EDXRF analyses. Especially Cu, Zn and Pb show error components from the decomposition process calling for careful homogenization before further standardization is attempted.

In any case, it should be tried to take greater sample portions for the decomposition to reduce the variability of AAS results; this cannot be accomplished with the procedure used here since 50 mg were the maximal sample amount that could be dissolved in the manner described under

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Experimental. An obvious solution to this problem could be the dissolution of the borax pellets[28] used for the EDXRF measurements, but this was not done in order to maintain the complete independence of the two methods.

Error components in EDXRF

The dependence of the EDXRF results on the sample portion is shown in Figures 1 and 3 for Fly Ash; they are normalized to the certified[2] or otherwise[24] published values.

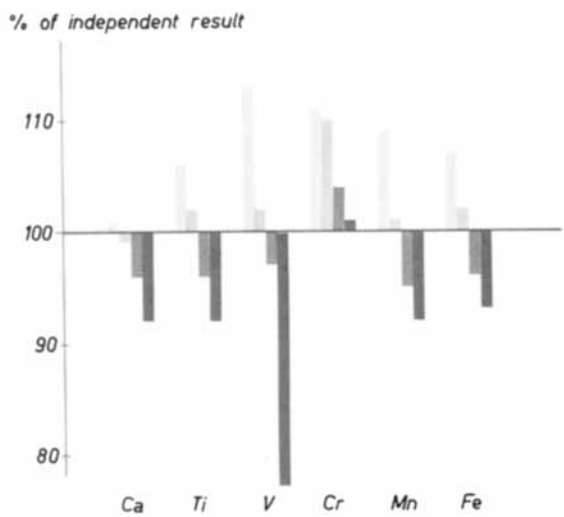

FIGURE 1 Comparison of median values of the EDXRF analyses of Fly Ash for increasing sample amount per glass bead.

The values are normalized to certified[2] or otherwise[24] published values.

- 0.25 g sample per glass bead
- 0.5 g sample per glass bead
- 0.75 g sample per glass bead
- 1.0 g sample per glass bead.

The determinations were performed with WO_3 as heavy absorber and Ni as secondary target.

Even though each sample portion (0.25, 0.5, 0.75 and 1.0 g) was represented by just one pellet and this pellet was measured just three times, some definite trends can be seen from this experiment: the medians of the three values tend to have the least deviation from the independent results for the pellets containing 0.5 g of the sample and this is the same

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amount of substance as was used for the preparation of the standards. In general, the content of glass beads containing less sample is biased too high, while the content of glass beads containing more sample is biased too low. Absorption effects which cannot be "buffered" sufficiently by the heavy absorber seem to be responsible for this. All subsequent analyses of urban dusts were run with 0.5 g of sample per glass bead.

Serious systematic errors can only be observed for Fe (if measured with Mo as secondary target), Ni, Cu and Sr. All four elements are fused with La_2O_3 as heavy absorber and measured with Mo as secondary target.

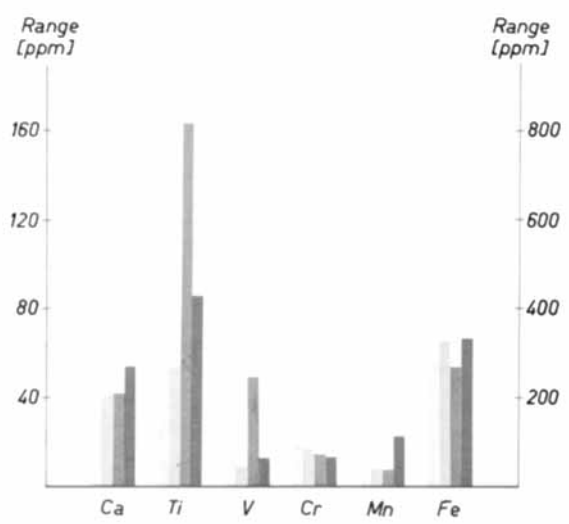

FIGURE 2 Range of values of the EDXRF analyses of Fly Ash for increasing sample amount per glass bead.

For detailed description see the caption of Figure 1. For Ca and Fe the scale is given on the right-hand side; for all other elements the scale on the left-hand side applies.

Nevertheless they deserve a separate discussion. The determination of Fe may be biased by uncorrected absorption effects. Ni and Cu, just barely detectable at these concentrations, show this systematic error because of an overestimation of the background which is a function of the Fe content in the borax bead: insignificant errors in the background calculations amount to a serious problem in quantitation. The Sr K_α-line, finally, is overlapping with the slop of the K_α incoherent Mo target scatter peak; this, too, makes the background correction highly unfavorable, possibly yielding biased results for Sr.

Figures 2 and 4 depict the range of the three parallel measurements and

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this can give additional information for the interpretation of the systematic deviations: the determination of Ni and possibly that for Cu appears to be limited by counting statistics for the dependence of the range from the sample amount per glass bead is apparent. For Ni the range is between 50% and 8% of the content, and for Cu it is about 20% to 15% of the content. The chosen reference value for Sr includes a serious uncertainty of ±300 ppm,[24] but other determinations give values

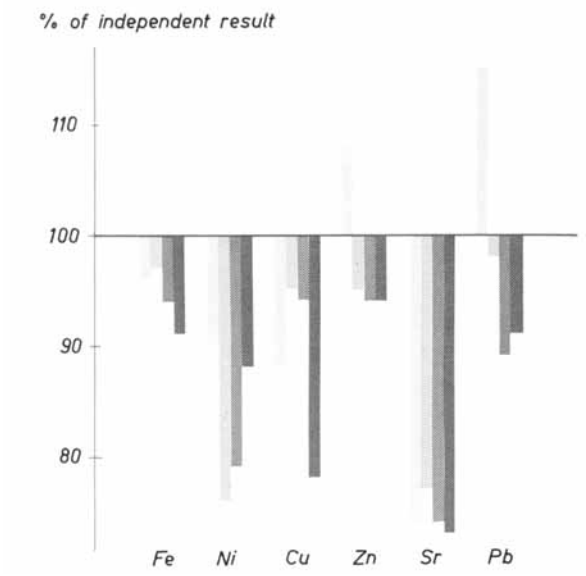

FIGURE 3 Comparison of median values of the EDXRF analyses of Fly Ash for increasing sample amount per glass bead.

The values normalized to certified[2] or otherwise[24] published values.

0.25 g
0.5 g
0.75 g
1.0 g
sample per glass bead

The determinations were performed with La_2O_3 as heavy absorber and Mo as secondary target.

of 1380 ppm[2] and 1300 ppm[29] which is much closer to the 1260 ppm reported here. Another element whose determination seems to be limited by counting statistics is Pb, but it has to be remembered that the Pb content in urban dusts is much larger than it is in Fly Ash (see Table V).

It also can be seen from Figures 2 and 4 that the determination of Fe is

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favorably accomplished with Ni as secondary target, as this gives a better precision of results.

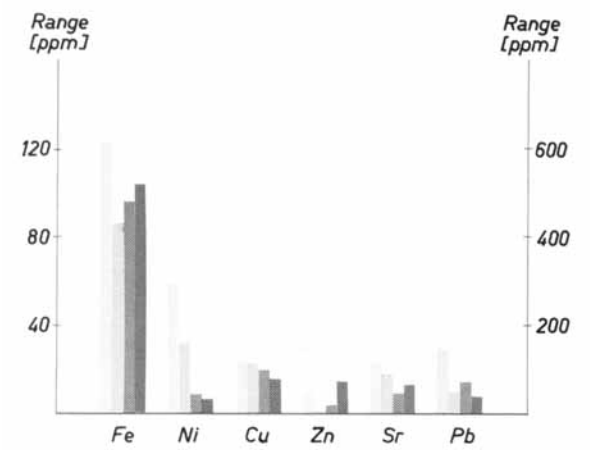

FIGURE 4 Range of values of the EDXRF analyses of Fly Ash for increasing amount per glass bead.

For detailed description see Figure 3.

For Fe the scale is given on the right-hand side; for all other elements the scale on the left-hand side applies.

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For the urban dust samples the estimate of basic instrument precision is listed in Tables VII and VIII; when these values are compared with the instrumental error of AAS it is obvious that they are much less dependent on the content of the elements. Within the limits of this study the precision of the elements Fe and Mn is better for the EDXRF than for the AAS. For Zn and Pb this seems to hold only for dust samples of high content.

The next question posed (see chapter on Experimental Design) concerning the fusing error introduced in the analysis; included in this error component is the variation caused by sample inhomogeneities. However, the tenfold increase in sample consumption for a borax pellet as compared to an acid decomposition tends to mask sample inhomogeneities. In fact, for the Graz dust significant variations could only be detected for Pb and for the Vienna dust for Cu, Pb, Sr and Fe (Table VII); for Fe the same inhomogeneity may occur in the Graz dust as well, but may not be detected because of an instrumental error more than twice as large (230 ppm vs 100 ppm). For the St. Louis dust the error due to the fusing procedure is detectable for Zn, Pb, Fe, Ca, Ti, Cr and Mn. Although the fusing error is always smaller for the borax bead preparation than it is for

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TABLE VII

Estimate of error components for the EDXRF analyses

Dust	Estimate of error due to	Fe	Cu	Ni	Zn	Pb_{L_α}	Pb_{L_β}	Sr
Graz	fuse	—	—	—	—	26^{xx}	24^{xx}	—
	instrument	230	9	11	10	11	6	4
Vienna	fuse	240^{xx}	10	—	—	—	19^{xx}	8^{x}
	instrument	100	10	11	10	6	6	4

All values are given in ppm and the error due to the fuse is significant at a confidence level of more than 0.1; one x indicates that the confidence level exceeds 0.05 an two x's indicate that the confidence level exceeds 0.01. All analyses were run using the molybdenum target and La_2O_3 as heavy absorber.

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TABLE VIII

Estimate of error components for the EDXRF analyses of St. Louis dust

Target and heavy absorber	Estimate of error due to	Ca	Ti	V	Cr	Mn	Fe	
	bag house section	—	—	—	—	—	—	
Ni/WO_3	fuse	1240^{xx}	76^{xx}	—	18^{xx}	12^{xx}	1140^{xx}	
	instrument	200	40	13	14	7	180	
		Fe	Cu	Ni	Zn	Pb_{L_α}	Pb_{L_β}	Sr
	bag house section	610	9	—	29	130^{xx}	110^{x}	—
Mo/La_2O_3	fuse	400^{xx}	—	—	40	14	60^{x}	—
	instrument	210	12	10	38	44	30	6

All values are given in ppm and the errors due to the bag house section and to the fuse are significant at a confidence level of 0.1; one x indicates that the confid level exceeds 0.05, two x's indicate that the confidence level exceeds 0.01. When no figure is given the error is not significant at a confidence level of 0.1.

the acid decomposition, for Pb (Graz), Cu (Vienna) and Cr (St. Louis) it is not reduced accordingly[26] indicating some inhomogeneities even within the borax bead. No further studies to elucidate the reasons were undertaken. Especially the WO_3 containing borax beads seem to include an appreciable error component introduced by the fusing step: no other explanation can be offered for the large error in the determination of Fe which is almost three times larger than that observed for the La_2O_3 beads (1140 ppm vs 400 ppm).

Table VIII gives the estimates of error due to the bag-house sampling procedure. No errors could be observed for the borax beads containing WO_3 as heavy absorber, but for the borax beads containing La_2O_3 Cu, Zn, Pb and Fe showed significant variations caused by the sampling procedure. Two facts seem to coincide: first, the WO_3 containing beads have more between beads variability making the between sections variability less readily detectable and, secondly, there is evidence that Cu, Zn and Pb are distributed more inhomogeneously than other elements. Substantial support for this hypothesis comes from a recent NBS study[30] that was performed on a homogenized St. Louis dust and gave for Cu, Zn and Pb values considerably different from the ones reported here.

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References

1. W. J. Youden, *Mat. Res. Stand.*, April 1961, p. 268.
2. National Bureau of Standards, Certificate of Analysis, Standard Reference Material 1633, Trace Elements in Coal Fly Ash, Washington, D.C., 1975.
3. K. F. J. Heinrich, K. E. Lorber and P. A. Pella, "X-ray Fluorescence Analysis of Environmental Samples by Borax Fusion", Paper presented at the EPA Symposium and Workshop on X-ray Fluorescence Analysis of Environmental Samples, January 1976, Chapel Hill, N.C., U.S.A.
4. P. A. Pella, D. N. Breiter, E. Kuehner, K. F. J. Heinrich and K. Lorber, "X-ray Fluorescence Analysis of Environmental and Botanical Samples by Means of Borax Fusion", Paper presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1977, Cleveland, OH, U.S.A.

5. K. E. Lorber, W. Wegscheider, H. Spitzy, K. F. J. Heinrich and P. A. Pella, "Development of EDXRF-Techniques for the Quantitative Multielement Analysis of Urban Dust Samples", Paper presented at the International Symposium on Microchemical Techniques, May 1977, Davos, Switzerland; published in *Mikrochimica Acta.* 1978I, No. 3–4.
6. P. A. Pella, K. E. Lorber and K. F. J. Heinrich, submitted to *Anal. Chem.*
7. W. Wegscheider, Dissertation, Technical University Graz, Austria, 1976.
8. A. L. Wilson, *Talanta* **17,** 21 (1970).
9. A. L. Wilson, *Talanta* **17,** 31 (1970).
10. A. L. Wilson, *Talanta* **20,** 725 (1973).
11. A. L. Wilson, *Talanta* **21,** 1109 (1974).
12. *Analytical Methods for Atomic Absorption Spectrophotometry* (Perkin-Elmer Corporation, Norwalk, Conn., U.S.A., Sept. 1976).
13. W. Wegscheider, G. Knapp and H. Spitzy, submitted to *Anal. Chim. Acta.*
14. F. J. Langmyhr and P. E. Paus, *Anal. Chim. Acta* **43,** 397 (1968).
15. F. J. Langmyhr and P. E. Paus, *Anal. Chim. Acta* **50,** 515 (1970).
16. L. Kotz, G. Kaiser, P. Tschöpel and G. Tölg, *Z. Anal. Chem.* **260,** 207 (1972).
17. A. M. Hartstein, R. W. Freedman and D. W. Platter, *Anal. Chem.* **45,** 611 (1973).
18. C. K. Matocha, "An Automatic Fusion Device for Preparation of Non-Metallic Samples for X-ray Fluorescence Analysis", Paper presented at the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, March 1974, Cleveland, OH, U.S.A.
19. R. L. Myklebust, C. E. Fiori, D. N. Breiter and K. F. J. Heinrich, "Data Reduction Procedure for Monochromatic X-ray Fluorescence Analysis with a Si(Li) Detector", National Bureau of Standards, Washington, D.C., 1977.
20. K. E. Lorber, "EDXRF Determination of Trace Amounts of Ti, V, Cr and Mn in a Fe-Ca-Si-Matrix", paper to be presented at the Euroanalysis III in Dublin, August 1978.
21. J. Mandel and T. W. Lashof, *ASTM Bulletin*, July 1959, p. 53.
22. C. A. Bennett and N. L. Franklin, *Statistical Analysis in Chemistry and Chemical Industry* (John Wiley & Sons, New York–London–Sydney 1967), pp. 319–465.
23. G. Retzlaff, G. Rust and J. Waibel, *Statistische Versuchsplanung* (Verlag Chemie, Weinheim 1975), pp. 83–98.
24. J. M. Ondov, W. H. Zoller, I. Olmez, N. K. Aras, G. E. Gordon, L. A. Rancitelli, K. H. Abel, R. H. Fliby, K. R. Shah and R. C. Ragaini, *Anal. Chem.* **47,** 1102 (1975).
25. W. B. Barnett, *At. Abs. Newsl.* **12,** 142 (1973).
26. B. Baule and A. Benedetti-Pichler, *Z. Anal. Chem.* **74,** 442 (1928).
27. A. D. Wilson, *Analyst* **89,** 18 (1964).
28. J. W. Owens and E. S. Gladney, *At. Abs. Newsl.* **15,** 95 (1976).
29. D. H. Klein, A. W. Andren, J. A. Carter, J. F. Emery, C. Feldman, W. Fulkerson, W. S. Lyon, J. C. Ogle, Y. Talmi, R. I. Van Hook and N. Bolton, *Envir. Sci. Technol.* **9,** 973 (1975).
30. P. A. Pella, National Bureau of Standards, personal communication.

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