AIR QUALITY INSTRUMENTATION

VOLUME 2

Edited by
J. W. Scales

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VOLUME 2

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FOREWORD

A primary objective of the Instrument Society of America is the dissemination of information describing advances in all phases of instrumentation. Air Quality Instrumentation, Vol. II is the second in a series of monographs containing air pollution related papers presented at recent ISA Conferences and Symposia.

This publication includes papers from the 1972 and 1973 ISA Annual Conferences, and various Division Symposia. The presentations include coverage of individual pollutant measurements, sample conditioners, calibration methods and devices, and data acquisition systems. Some papers deal with new concepts, while others describe the modification or refinement of existing instrumental techniques. Subject and author indexes are provided for the convenience of the reader.

Recognition must be given to the session developers, committee chairman and officers of the ISA and its Divisions for their untiring work in developing the conference and Symposia programs from which these papers were taken. The assistance of the ISA Headquarters staff in handling the myriad of details involved in a publication of this type is also gratefully acknowledged.

Special recognition and appreciation must be extended to the authors for their untiring effort and dedication in preparing the papers which are the basis of this publication.

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ENERGY DISPERSIVE X-RAY EMISSION SPECTROMETRY FOR MULTIELEMENT ANALYSIS OF AIR PARTICULATES*

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INTRODUCTION

Environmental specialists are concerned not only with the total amount of particulates in the air but also with their chemical composition. Multi-element analysis is necessary for revealing and identifying air particulate pollution sources. For routine, multi-element analysis of large numbers of air particulate samples the analytical technique must be rapid and inexpensive. If such a technique were available, surveillance could be established over wide areas where air pollution is a problem.

Conventional analytical techniques such as gravimetry, colorimetry, emission spectroscopy or atomic absorption spectrophotometry can provide the required sensitivity for detection of most metallic element air pollutants, but they are time and labor consuming. An experienced analyst is required to perform the determinations even when done routinely. The original sample cannot be preserved for repeat analyses since it must be dissolved. Besides, the necessary wet chemical sample preparation is an additional source of errors.

Emission spectroscopy [1] and atomic absorption spectrophotometry[2] are at

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present the most widely used methods in air pollution control laboratories. Emission spectroscopy is a multi-element technique but requires careful sample pretreatment and is generally considered to be less precise. Also, preparation of standards requires considerable care and effort.

Atomic absorption spectrophotometry is strictly a single element technique, but modern instruments have interchangeable lamps for sequential analysis of up to six elements per sample. A standard 20.3 x 25.4 cm (8 x 10 in.) air particulate filter may not be large enough for sequential determinations of many elements, especially when the more accurate method of standard addition is used.

The sensitivities of both these techniques vary significantly from element to element. In fact emission spectroscopy has insufficient sensitivity for such important potential pollutants as Se, Hg, As and Cd, and atomic absorption for As, Hg and Se.

Several papers have been published on the application of neutron activation for the analysis of air particulates.[3-5] Again, the technique is very sensitive for some elements while quite insensitive for others (in particular, lead). In order to cover the range of elements of interest in air pollution control, access to a nuclear reactor is necessary, and a long time between sample irradiation and measurement must be allowed (from several hours up to a few weeks for some elements).[3] Neutron activation analysis can be used in special cases but is rather impractical for routine application.

X-ray fluorescence spectroscopy has been used for air particulate analysis by a few workers.[6,7] However, the conventional method, using an x-ray tube, a crystal spectrometer and sequential counting of each element, has not found broad application in the routine air particulate analysis.

The automatic, energy dispersive system with an Si(Li) detector and radioisotope sources, used in this work, has all the features required for routine, multielement air particulate analysis of large numbers of samples. No sample preparation is necessary beyond cutting a 5 cm (2 in.) diameter piece out of the filter paper sample collector. The measurements are simultaneous for all the characteristic x-rays excited, and the method is nondestructive. Once loaded with samples, the apparatus can operate unattended.

X-RAY FLUORESCENCE ANALYSIS OF THIN SPECIMENS

The technique of measuring thin specimens is not new in conventional (wavelength dispersive) x-ray fluorescence spectrometry.[8] However, little work has as yet been reported on its use in energy dispersive x-ray spectrometry, although its advantages are more numerous in this case.[9]

The main advantages of measuring thin specimens are as follows. Matrix effects are reduced or eliminated; the characteristic x-ray intensity is a linear function of the element mass per unit area, over several orders of magnitude; and the fluorescent to scattered ratio can be much increased compared with that of a

thick specimen.[9] Furthermore it can be shown that, for air particulates on filter papers, errors due to the particulate nature of the specimen are small and are simple functions of the grain size of the fluorescing particles only.[10]

Thin Specimen Criterion

Assuming both the incident and emitted x-rays are normal to the specimen and the penetration of the x-rays into the specimen is small compared with the source-specimen and specimen-detector distance, it can be shown that the fluorescent x-ray intensity I_f from an element x is[11]

$$I_f = kI_o \frac{(\omega \tau r)_x}{(\mu_1 + \mu_2)} [1\text{-exp-}(\mu_1 + \mu_2) \text{ counts/s}] \quad (1)$$

where:

- k is a geometrical constant, and includes the detector efficiency and absorption in windows
- I_o is the source emission (photons/s)
- ω is the fluorescence yield for the x-ray transition excited (i.e., ω_K or ω_L)
- τ is the photoelectric cross section for that transition, at the source energy (cm^2/g)*
- r is the weight fraction of element x
- μ_1 is the total mass absorption coefficient for the sample (summed over all elements) at the source energy (cm^2/g)*
- μ_2 is that at the characteristic x-ray energy; and
- m is the sample mass per unit area (g/cm^2)

The normal incidence assumption is a good approximation for the broad beam geometry used in radioisotope x-ray spectrometry.[11] The assumption of low penetration is good at all energies for thin specimens.

For specimens that are considered thin according to the criterion given below, the exponential in Equation 1 can be expanded to its linear term and the expression for fluorescent intensity simplified to

$$I_f = kI_o \omega \tau r_x m \quad (2)$$

That is, the fluorescent x-ray intensity is directly proportional to the mass per unit area of the element present ($r_x m$ g/cm^2). The term $(\mu_1 + \mu_2)$, which represents matrix interferences due to self-absorption of the fluorescent x-rays by other elements in the sample, cancels out. Similarly, interferences due to enhancement of the measured fluorescent intensity by other characteristc x-rays excited in the sample, disappear.

*If the source emits more than one significant energy, these coefficients vary and Equations 1 and 2 must be summed over all values.

A thin specimen is defined [11,12] as having a value of $(\mu_1 + \mu_2)$ m such that the fractional error in I_f caused by using Equation 2 instead of Equation 1 is less than a certain value, say 0.05. There is no sharp dividing line between "thin" and "thick" specimens, but a suitable criterion is

$$m \leq \frac{0.1}{(\mu_1 + \mu_2)} \tag{3}$$

when the abovementioned fractional error is ≤ 0.05.

All the air particulate samples measured in this work were found to have values of deposit mass per unit area well below those required for conformity with the thin specimen criterion. For example, the critical value calculated for Fe K x-rays excited in a deposit consisting of 95% sand is 1600 $\mu g/cm^2$ whereas the average mass per unit area of the actual deposits was found to be 370 $\mu g/cm^2$.

Fluorescent to Backscattered Ratio

The ratio of fluorescent intensity (I_f) from a given element, to the intensity of source radiation backscattered from the whole sample (I_s) is much larger for thin specimens than for infinitely thick ones. In fact

$$\frac{(I_f/I_s)_{thin}}{(I_f/I_s)_{thick}} = \tfrac{1}{2}\left[1 + \frac{\mu_2}{\mu_1}\right] \tag{4}$$

Usually the exciting energy is about twice the fluorescent energy, in which case $\mu_2 \simeq 7\mu_1$, and the fluorescent to backscattered ratio for thin specimens is then four time that for thick ones.

In energy dispersive x-ray spectrometry there are two major reasons for maximizing the fluorescent to backscattered ratio. The first is associated with the degradation of detector performance and escalating dead time losses at high count rates. Usable count rates are limited by these factors to about 10^4/s, and since sources are available that yield such count rates even with thin specimens, this represents a practical limit to the sensitivity of the technique. In this case $(I_f + I_s)_{thick}$ is limited by the detector to the same value as $(I_f + I_s)_{thin}$. Since near the limit of detection for a given element, I_f is negligible compared to I_s, $(I_s)_{thick} = (I_s)_{thin}$ and equation (4) becomes

$$\frac{(I_f)_{thin}}{(I_f)_{thick}} = \tfrac{1}{2}\left[1 + \frac{\mu_2}{\mu_1}\right] \tag{5}$$

In other words the use of thin specimens allows an increase in signal by a factor of $\tfrac{1}{2}(1 + \mu_2/\mu_1)$.

The second reason is associated with the background under the fluorescent peaks, which is mainly due to incomplete charge collection in the detector and, therefore, results largely from detection of the backscattered radiation. Al-

though the incorporation of guard rings in detectors can reduce this background by large factors,[13] it is still the main background, so the use of thin specimens is still advantageous in reducing it.

Particle Size Effects

Particle size effects are caused by significant absorption or enhancement of the required fluorescent radiation within a single grain. Even though the average mass per unit area of the particulate deposit conforms to that for a thin specimen, individual grains may still be large enough to produce these effects. The most recent theory of particle size effects has been put forward and experimentally verified for "infinitely thick" specimens.[14] We are at present investigating its extension to specimens of any thickness.[10] It can be shown that for air particulates collected on filter papers the following simplified formula holds[10]

$$I'_f = kI_o \omega \tau r_x m. \frac{[1-\exp-(\mu_f + \mu'_f)d]}{(\mu_f + \mu'_f)d} \qquad (7)$$

where d is the particle size (cm), and μ_f and μ'_f the linear attenuation coefficients of the fluorescent grains at the exciting and fluorescent energies (cm^{-1}).

The main assumption is that the volume concentration of fluorescent grains is very small ($\lesssim 0.01$), which is certainly true for the air particulate samples analyzed here. It is seen that there are no inter-particle effects; that is to say, the fluorescent intensity for a given element is affected only by the size of the grains containing that element. Also the reduction in intensity is a simple and, to a first approximation, linear function of grain size. These two results represent extremely important simplifications of the usually very complex effects and enable the particle size effect to be incorporated in the calibration factor for that element. Calculations show that the factor $\frac{[1-\exp-(\mu_f + \mu'_f)\ d]}{(\mu_f + \mu'_f)\ d}$ remains within 10% of unity for almost all the element/grain size combinations encountered in the present work.

EQUIPMENT

The analytical system used in this work is shown schematically in Figure 1 and consists of the following main components: automatic sample and source changer with capacities of thirty samples and four sources respectively;[a] three annular radioisotope source assemblies[b] (Fe-55, 120 mCi; Pu-238, 400 mCi and Cd-109, 12 mCi); one 80 mm^2 x 4 mm thick Si(Li) detector and FET preamplifier with pulsed optical feedback, cooled by liquid nitrogen and having a resolution of 180 eV (FWHM) at 5.9 keV;[c] electronic circuitry detailed below; and a minicomputer[d] with teletype terminal.

a. Manufactured by Columbia Scientific Industries.
b. Amersham-Searle Models IEC-K-359, PPC-5 and CUC-3, respectively.
c. KeVex Corp. Model 3000P.
d. Nova, with software supplied by Applied Computer Systems Division of Columbia Scientific Industries.

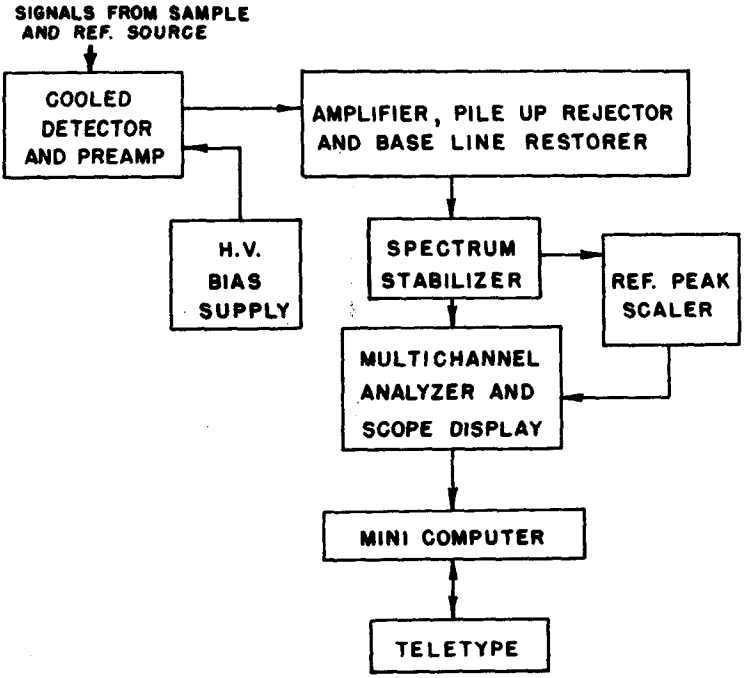

Figure 1. Schematic of radioisotope x-ray fluorescence analytical system.

The electronic circuitry consisted of the following modules: high voltage supply and amplifier with baseline restorer and pile up rejector;[e] spectrum stabilizer set on a reference peak located at the high energy end of the spectrum range; [f] scaler with preset count;[g] analog to digital converter with 1024 channel analyzer and scope display.[h] The baseline restorer with pile up rejector is needed to preserve the spectrometer resolution at count rates above 1000 counts/s. However, the resultant high dead time causes the percentage of lost counts to vary significantly with the total detected count rate. These losses are not corrected for by the live time meter of the multi-channel analyzer.

In order to provide accurate timing at high count rates, the peak from the reference source is monitored by the scaler. The accumulation of the x-ray spectrum is stopped by the scaler after a preset count is obtained in the refer-

e. KeVex Corp. Model 4000.
f. Canberra Industries Model 1520.
g. Mechtronics Nucler Model 701.
h. Northern Scientific Models NS-622 and NS-636.

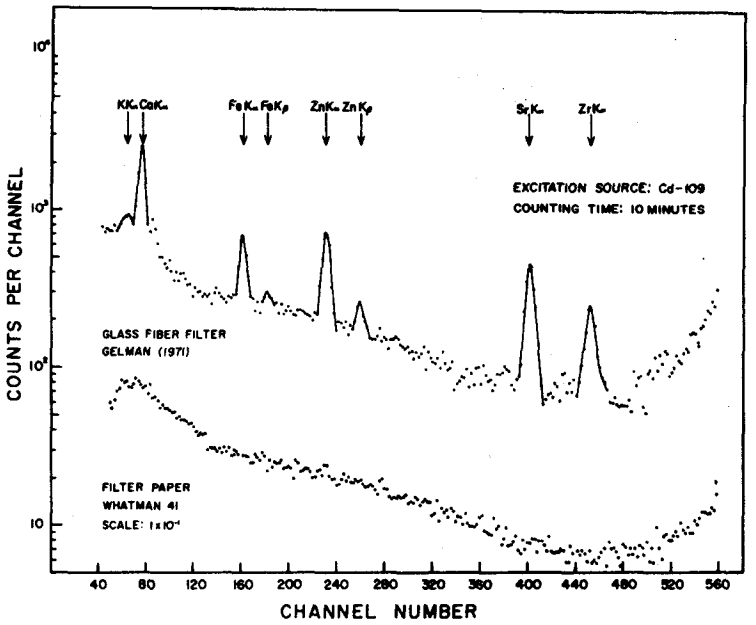

Figure 2. X-ray fluorescence spectra of glass fiber and paper filters.

ence peak. The radioisotope used in the reference source is Am-241 which has a half life of 450 years.

EXPERIMENTAL

Sampling Procedure

The particulate samples obtained for this study were collected on 20.3 x 25.4 cm Whatman 41 filter paper over 24-hour periods using standard high volume samplers.

The cellulose filters used are essentially free of contamination whereas the standard glass fiber filters contain appreciable quantities of zinc, iron, zirconium, potassium, calcium and strontium, rendering them quite unsuitable for the direct analysis methods used here. Figure 2 shows a spectrum from a blank fiber glass filter paper compared with one from Whatman 41. The source used was Cd-109.

In order to eliminate errors due to hygroscopicity of the cellulose filters, they were stored for 24 hours in a constant humidity box before each weighing, and weighed a fixed time (7 minutes) after removal from the box.

Two sets of samples were collected, the handling procedure being the same in each case. The filters were numbered, stored in the humidity box, weighed and mailed to the sampling station. The samples were collected on the specified day

and the filters mailed back, stored in the humidity box, reweighed and analyzed for 17 elements using the automatic energy dispersive x-ray spectrometer. Subsequently, 12 of the samples were analyzed for 6 elements each by atomic absorption spectrophotometry[a] for comparison purposes.

The first set of 38 samples was collected on the same day in June 1971 at 38 stations distributed between rural and urban areas throughout the State of Texas. The second set of 51 samples was collected at one city, Corpus Christi, in three batches of 17 on three specified days in July 1971.

Method

Specimens in the form of 47 mm diameter discs were cut out of the original filter papers and measured in batches of 27, along with three standards. In order to obtain the best excitation efficiencies, the 17 elements to be determined were divided into three groups, each excited by one of the sources. Ca, Ti and V were excited by Fe-55; Cr, Mn, Fe, Co, Ni, Cu and Zn by Pu-238; and Hg (L x-rays), Pb (L x-rays), As, Br, Sr, Zr and Mo by Cd-109. Each batch of specimens was counted with each of the three sources. The counting period was that required to accumulate 200 000 counts in the reference peak, which amounted to about 10 minutes per specimen with Pu-238 and Cd-109, and 5 minutes with Fe-55.

The computer program was designed for automatic operation of the sample and source changers and of the spectrometer system. Groups of channels (i.e., "windows") were preset for K_α and K_β or L_α and L_β peaks of each element to be determined and for backgrounds between peaks. The data processing part of the program was designed to integrate peak and background areas, subtract backgrounds from total peaks, subtract superimposed α- or β-peaks of adjacent elements using K_α/K_β and L_α/L_β ratios predetermined from multielement standards, and calculate element concentrations using calibration factors obtained from the standards. Element concentrations were printed out in $\mu g/cm^2$ of filter paper and in $\mu g/m^3$ of air.

Standards

Since for thin specimens the characteristic x-ray intensity is a linear function of the concentration of the emitting element over a wide range of concentrations, we used in this work single calibration factors for each element. The calibration factors were calculated from multi-element standards with concentrations of the main elements similar to those in real air particulate samples. K_α/K_β and L_α/L_β ratios were also obtained from the same standards. Each standard contained 200 $\mu g/cm^2$ of Ca, 20 $\mu g/cm^2$ of Fe, 5 $\mu g/cm^2$ each of Pb and Br and 1 $\mu g/cm^2$ of 3 to 5 other elements. The elements present in a given standard were selected so as to avoid spectral interferences. The standards were prepared from solutions containing mixtures of elements in the desired concentrations uniformly deposited on Whatman 41 filter paper discs.

a. Using a Bausch and Lomb Model AC2-20 Atomic Absorption Spectrophotometer.

The quality of analytical results depends on the accuracy of standards used. An ideal standard would be a filter paper with a collected air particulate deposit analyzed by several independent laboratories using reliable methods of analysis (such as "standard reference materials" prepared by the NBS). This is, however, difficult to achieve since air particulates vary very much in elemental composition and particle size distribution. We chose standards made up from solutions because this was the easiest way to obtain all the desired combinations of elements in the appropriate concentrations. That differences in particle size between standards and unknowns did not cause appreciable errors is evidenced by the good agreement between the x-ray fluorescence and atomic absorption results.

However, work is in progress on the development of methods of preparing standards having controlled particle size distributions.

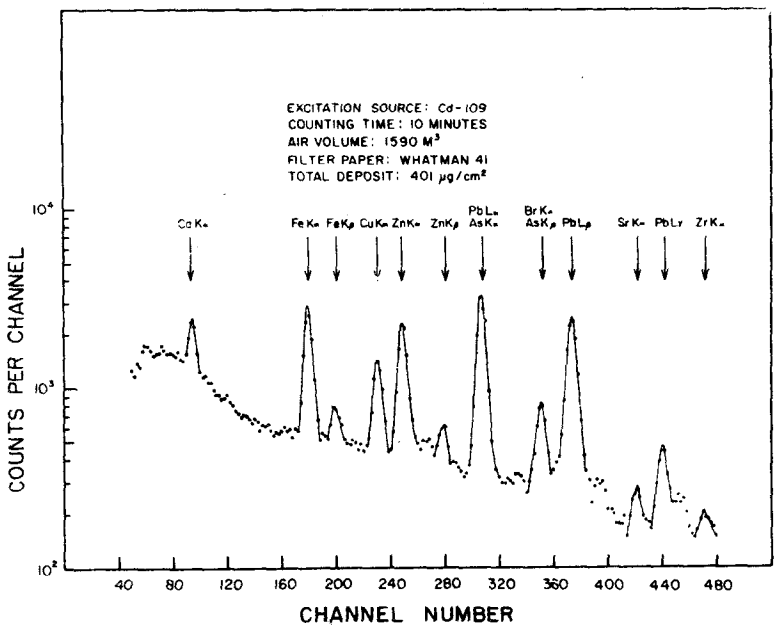

Figure 3. X-ray fluorescence spectrum of air particulate sample from West Texas.

RESULTS AND DISCUSSION

Results

Figure 3 shows a typical x-ray spectrum obtained.

TABLE I

Selected results of X-ray fluorescence analyses

($\mu g/m^3$)

Location	Ca	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Hg	Pb	As	Br	Sr	Zr	Mo
Amarillo	2.7	0.34	<0.006	0.01	0.05	1.5	<0.02	<0.01	0.12	0.15	<0.03	0.32	<0.01	0.09	0.01	0.01	0.01
Beaumont	18.3	0.10	<0.011	0.06	0.04	0.4	<0.03	<0.02	0.23	0.01	0.05	0.44	0.01	0.16	0.02	<0.01	0.02
Clute	29.9	0.22	<0.007	0.01	0.01	1.0	<0.02	<0.01	0.01	0.11	<0.03	0.60	<0.01	0.11	0.05	0.01	<0.007
Corpus Christi	21.9	0.29	<0.008	1.10	0.09	10.0	<0.02	<0.01	0.16	1.77	<0.03	0.80	0.01	0.07	0.04	<0.008	0.01
El Paso	13.7	0.34	<0.008	<0.06	0.11	3.4	<0.02	<0.01	0.96	1.66	<0.03	2.56	0.09	0.25	0.03	<0.008	0.02
Fort Worth	17.7	0.20	<0.008	<0.07	0.05	1.3	<0.02	<0.01	0.01	0.23	<0.03	0.54	<0.01	0.19	0.02	<0.008	0.01
Harlingen	11.8	0.20	<0.006	<0.05	<0.03	1.2	<0.02	<0.01	0.02	0.02	<0.03	0.04	<0.01	0.02	0.01	<0.006	<0.006
Lubbock	8.5	1.33	<0.006	<0.05	0.17	8.6	0.05	<0.01	0.01	0.05	<0.03	0.26	<0.01	0.08	0.04	0.05	<0.006
Dallas	4.8	0.08	<0.004	0.01	0.01	0.7	<0.01	<0.01	0.02	0.01	<0.02	0.67	<0.01	0.24	0.01	<0.004	<0.004
Houston	6.6	0.11	<0.008	0.05	<0.03	0.6	<0.03	<0.01	0.22	0.14	<0.03	1.03	<0.01	0.47	<0.01	<0.008	<0.008
Matagorda	0.8	0.04	<0.005	<0.04	<0.02	0.2	<0.01	<0.01	0.36	<0.005	0.03	0.04	<0.01	<0.03	<0.007	<0.005	<0.005
San Antonio	3.5	0.12	<0.004	<0.04	<0.02	0.1	<0.01	<0.01	<0.01	0.07	<0.02	0.33	<0.01	0.10	<0.006	<0.004	0.10

Table I shows x-ray fluorescence data for all elements determined, from selected locations, expressed in μg element per m^3 air.

Table II compares some of the atomic absorption and x-ray fluorescence data for several samples from the first series. The five elements compared are those determined by both methods and found in appreciable concentrations.

TABLE II

COMPARISON OF RESULTS OF X-RAY FLUORESCENCE AND ATOMIC ABSORPTION ANALYSIS

($\mu g/m^3$)

	Mn		Fe		Cu		Zn		Pb	
	AA	X-Ray	AA	X-Ray	AA	X-Ray	AA	X-Ray	AA	X-Ray
Amarillo	0.02	0.05	1 48	1.5	0.10	0.12	0.20	0.15	0.35	0.32
Beaumont	0.03	0.04	0.65	0.4	0.13	0.23	0.11	0.01	0.46	0.44
Clute	0.03	0.01	0.98	1.0	0.03	0.01	0.13	0.11	0.55	0.60
Corpus Christi	0.08	0.09	4.41	10.0	0.16	0.6	1.37	1.77	0.75	0.80
El Paso	0.10	0.11	2.61	3.4	0.89	0.96	1.55	1.66	2.73	2.56
Forth Worth	0.05	0.05	1.53	1.3	0.01	0.01	0.69	0.23	0.66	0.54
Harlingen	0.02	<0.03	1.24	1.2	0.02	0.02	0.20	0.02	0.12	0.04
Lubbock	0.16	0.17	2.59	8.6	0.03	0.01	0.22	0.05	0.34	0.26
Dallas	0.01	0.01	0.75	0.7	0.02	0.02	0.10	0.01	0.66	0.67
Houston	0.02	<0.03	0.65	0.6	0.22	0.22	0.19	0.14	0.92	1.03
Matagorda	NA	<0.02	0.28	0.2	0.31	0.36	0.37	<0.005	0.08	0.04
San Antonio	0.01	<0.02	0.62	0.1	0.06	<0.01	0.51	0.07	0.46	0.33

Table III compares values of arithmetic mean elemental concentrations found in this work with some of the (sparsely) available published data. More detailed results are quoted and discussed elsewhere.[15]

The validity and accuracy of the results are supported by: a) the extremely good agreement (Table II) between our method and one currently accepted, viz., atomic absorption; and b) the general agreement between the various average values given in Table III even though the places and times of sampling, and the averaging periods, differ drastically.

Although the present survey was intended as a test of the technique rather than a search for pollution sources, two hitherto unknown sources were revealed, and several elements and element combinations were found to correlate with possible types of pollution. In this preliminary study the most interesting elements were Ca, Ti, Cr, Fe, Cu, Zn, Pb, As, Br and Mo. The low values for V and Ni are noteworthy in view of their importance as pollutants in certain other areas of the country. Mercury in particulates was generally undetectable.

Almost all the samples contained lead and bromine in amounts correlated with