TRACE ELEMENTS IN CALIFORNIA AEROSOLS PART 1. INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS TECHNIQUES

R. C. Ragaini
H. R. Ralston
D. Garvis
R. Kaifer

June 18, 1975

Prepared for U.S. Energy Research & Development
Administration under contract No. W-7405-Eng-48

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Printed in the United States of America
Available from

National Technical Information Service
U. S. Department of Commerce
5285 Port Royal Road

Springfield, Virginia 22151

Price: Printed Copy \$ *; Microfiche \$2.25

<u>* Pages</u>	<u>NTIS Selling Price</u>
1-50	\$4.00
51-150	\$5.45
151-325	\$7.60
326-500	\$10.60
501-1000	\$13.60

LAWRENCE LIVERMORE LABORATORY
University of California - Livermore, California 94550

UCRL-51850

**TRACE ELEMENTS IN CALIFORNIA AEROSOLS
PART I. INSTRUMENTAL NEUTRON ACTIVATION
ANALYSIS TECHNIQUES**

Final Report

California Aerosol Characterization Experiment
1972-1974

R. C. Ragaini
H. R. Ralston
D. Garvis
R. Kaifer

MS. date: June 18, 1975

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Foreword

This report will be included in Volume II of the final report, "Characterization of Aerosols in California (ACHEX) Study," submitted to the Air Resources Board of the State of California as Rockwell International Science Center Report SC524.25FR, September, 1974. This LLL report was prepared for the Air and Industrial Hygiene Laboratory of the California State Department of Public Health under Agreement Number 601.

Part I consists of a description of the procedures used for Instrumental Neutron Activation Analysis (INAA), validation tests, analyses of blank, and sample data.

Part II includes presentations of the episodic data for Phase I and II, the elemental diurnal patterns and size distributions. Analyses of the background site data and the source-enriched site data are used to discuss the sources of the trace elements and the various physical and chemical processes during aerosol transport. Also included are preliminary Lundgren impactor validation studies to evaluate the bounce-off problems with various substrates and to evaluate wall-loss effects.

Some of the data contained in this report has already been discussed in preliminary form in several reports and presentations:

1. R. Ragaini, R. Kaifer, and J. J. Wesolowski, "A Report on Neutron Activation Analysis in ACHEX-I," Air and Industrial Hygiene Laboratory (AIHL) Report No. 130 (September 1972).
2. J. J. Wesolowski, B. R. Appel, A. E. Alcocer, P. K. Mueller, R. Ragaini, and R. Kaifer, "Chemical Measurements of California Atmospheric Aerosols," AIHL Report No. 154 (October 1973).
3. B. R. Appel, J. J. Wesolowski, A. Alcocer, S. Wall, S. Twiss, R. Giauque, R. Ragaini, and R. Ralston, "Quality Assurance for the Chemistry of the Aerosol Characterization Experiment," AIHL Report No. 169 (July 1974).
4. J. J. Wesolowski, P. K. Mueller, B. R. Appel, S. Wall, A. E. Alcocer, R. Giauque, T. Novakov, R. C. Ragaini, and R. Kaifer, "Sampling and Chemical Analysis Results," American Chemical Society National Meeting, Chicago, August 1973.
5. J. J. Wesolowski, B. R. Appel, A. E. Alcocer, P. K. Mueller, R. C. Ragaini, and R. Kaifer, "Chemical Measurements of California Atmospheric Aerosols," GAF Gesellschaft für Aerosolforschung Conference, Bad Soden, Germany, October 1973.
6. R. C. Ragaini, R. Kaifer, and J. J. Wesolowski, "The Role of Neutron Activation Analysis in the California Aerosol Characterization Study," Pacific Conference on Chemistry and Spectroscopy, San Diego, November 1973.
7. R. C. Ragaini, "Air Pollution Research Objectives Using Trace Element Analyses," NSF Workshop on Nuclear Techniques for Environmental Trace Element Information Relative to Energy Production and Consumption, Tallahassee, Florida, June 24-26, 1974, UCRL-75862.

8. R. D. Giauque, Lilly Y. Goda, and R. C. Ragaini, "Chemical Characterization of California Aerosols by Elemental Analysis," 167th American Chemical Society Conference on Chemistry and Spectroscopy, Los Angeles, California, April 1974.
9. B. R. Appel, J. J. Wesolowski, G. M. Hidy, R. D. Giauque, and R. C. Ragaini, "The Chemistry of California Atmospheric Aerosols," Pacific Conference on Chemistry and Spectroscopy, San Francisco, California, October 1974, UCRL-75863.

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TRACE ELEMENTS IN CALIFORNIA AEROSOLS PART 1. INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS TECHNIQUES

Abstract

Instrumental Neutron Activation Analysis (INAA) done at LLL played a key role in the 1972-1974 California Aerosol Characterization Experiment (ACHEX), a major experiment in the chemistry of aerosols in urban and non-urban sites of California sponsored by the State of California Air Resources Board. The main purpose of INAA was to measure the particle size distributions and diurnal patterns of key chemical constituents in aerosols collected in California. These data were used to satisfy some of the key objectives of ACHEX, including aerosol

characterization and evaluation of the origins and evolutions of aerosols.

Secondary uses of INAA were the validations of the Lundgren rotating drum cascade impactors used in the ACHEX, and validations of other analytical techniques used in the chemical analyses.

As a result of these studies, it was concluded that techniques using INAA were useful operational methods for chemical analysis of aerosols collected over two-hour periods in urban air with an active monitoring program.

Introduction

Recognizing that the origins and evolution of atmospheric aerosols were poorly understood, the California Air Resources Board (ARB) sponsored a major experiment in the chemistry of aerosols in urban and non-urban sites of California during 1972-1974.

The first phase of the study (ACHEX-I) emphasized the gathering of a wide variety of data characterizing atmospheric aerosols sampled in late summer and fall of 1972. The second phase (ACHEX-II) was primarily concerned with smog aerosols in the South Coast Air Basin during 1973.

The objectives of ACHEX-I were:

- To characterize the aerosols in the South Coast, the San Francisco Bay Area, and the San Joaquin Valley Basins in terms of their physical and chemical properties, interaction with atmospheric gases, and natural and anthropogenic origins.
- To evaluate the amount of atmospheric aerosol in the cited three major air basins which can be related to: (1) primary emissions such as from auto exhausts or smokestacks; and (2) secondary

production due to physical and chemical processes taking place in the atmosphere.

- To identify those major sources of particles and chemically reactive gases which can be related to aerosol pollution and visibility reduction.
- To estimate from aerosol source characterization in the three major regions the extent to which the ambient air quality standards can be achieved by existing technology.
- To evaluate the applicability of the aerosol analysis instrumentation employed in this study for use in other monitoring networks.

The objectives of ACHEX-II were:

- To characterize aerosols in the South Coast Basin in terms of their physical and chemical properties and their interaction with atmospheric gases.
- To improve knowledge of secondary aerosol formation processes by investigating the evolution of aerosols under conditions of photochemical smog formation.
- To estimate the primary and secondary aerosol contributions to the total airborne particulate concentration in the South Coast Basin.
- To evaluate the significance of anthropogenic sources and uncontrollables, including meteorological factors, natural sources, and water, in the evolution of the respirable and visibility degrading aerosol.
- To recommend from the characterization of aerosols and their sources the key ingredients for a control strategy in the South Coast Basin.

- To evaluate the applicability of instrumentation employed in this study for use in future monitoring programs.

The program was managed by the Science Center Rockwell International; it directly involved the California Air and Industrial Hygiene Laboratory, California Institute of Technology, Meteorology Research Inc., the Statewide Air Pollution Research Center (SAPRC) of the University of California, Riverside, the University of Minnesota, Thermo-Systems, Inc., Lawrence Berkeley Laboratory, Lawrence Livermore Laboratory, the University of Washington, the ARB El Monte Laboratories, and the Bay Area Air Pollution Control District (BAAPCD).

The ACHEX was designed to achieve its objectives through intensive and detained episodic measurements of aerosol behavior in the presence of trace gases and meteorological changes.

Generally, each run in the field experiment consisted of a 24-hour period. The operations were selected on the basis of an aerometric forecast one day ahead of startup. The run periods were selected mainly on the basis of conditions conducive to high levels of air pollution. In the South Coast Basin, runs were planned for oxidant levels exceeding 0.20 ppm, except for source-dominated cases.

The intensive acquisition of data took place during a two-year period from 1972 to 1973, with most of the activity concentrated in the late summer and early fall to cover times of highest photochemical smog intensity, as measured by elevated oxidant concentrations. The keystone of the measurement program was a mobile laboratory equipped with a variety of

instrumentation. The mobile unit was moved to several different sites during the course of the field studies. Sites were selected to provide key information on: (1) source-dominated air, (2) receptor cases where pollutants were mixed and had reacted for a period of time, or (3) non-urban locations potentially characteristic of marine, desert, or photochemical background contamination.

The mobile laboratory operations were supplemented by fixed stations. In ACHEX-I (1972), these stations were at the Keck Laboratories at Caltech, the SAPRC monitoring station at Riverside, and the BAAPCD station in San Jose. During the 1973 phase, the fixed stations were replaced in the South Coast Basin by a modification of four district air-monitoring stations. These included the LAAPCD stations at downtown Los Angeles and Pomona, the ARB station in Riverside, and the OCAPCD station in Anaheim.

A key element of the ACHEX was the extensive chemical analysis undertaken on selected aerosol samples during the course of the experiment. Samples for study were chosen on the basis of priority for the intensity of air pollution observed, or in terms of other information required to meet the objectives of the program.

Many of the chemical methods used in ACHEX required levels of sensitivity that exceeded routine procedures in the past. Therefore, considerable development of methods was undertaken, including neutron activation analysis (NAA), x-ray fluorescence analysis (XRFA), photoelectron spectroscopy (ESCA), high-resolution spectroscopy, atomic absorption (AAS), and wet chemical methods for non-carbonate carbon, sulfate, nitrate,

and liquid water content. Our group at Lawrence Livermore Laboratory was responsible for carrying out the INAA measurements.

In the ACHEX, more than 3000 samples of aerosols were collected during 1971-1973 and INAA was utilized to non-destructively analyze the particulates on 700 samples including Whatman 41 high-volume filters, Gelman 5- μ GA-1 cellulose-acetate, low-volume total filters and filters after Lundgren^{*} rotating drum cascade impactors. Various impactor films were used and analyzed in the experiment: Mylar, Teflon, sticky-resin-coated polyethylene, and paraffinated Mylar. The only collection media not studied were glass fiber and silver membrane filters.

The normal procedure was to cut out sections of the substrate and perform INAA as well as XRFA for elemental analyses. Although INAA and XRFA are complementary techniques for trace-element analyses because of differing elemental detection sensitivities, a number of elements are measured in both techniques such as Fe, Br, V, Mn, and Ca. Interlab comparisons were made to validate the elemental analyses, and the agreements were quite satisfactory. The comparison did point out the importance of validation in an environmental program, especially when chemical analyses are performed by different methods. The data were transmitted to AIHL on IBM punch cards for computer data bank storage and later analysis.

^{*}Reference to a company or product name does not imply approval or recommendation of the product by the University of California or the U. S. Energy Research & Development Administration to the exclusion of others that may be suitable.

The strategy for determining the sources of the aerosols was based on measurements of the key chemical constituents as shown in Table 1. INAA played a significant role because of its ability to determine a large number of the chemical constituents of interest. Therefore, NAA could detect elements indicative of windblown dust such as Al and rare earths (not shown), elements indicative of

marine aerosols such as Na and Cl, and elements introduced by man such as Br, V, Zn, and Se. The elements detected by INAA are marked with an asterisk.

As discussed in more detail later, two irradiations and four different counts were involved in the analyses. The LLL 3-MW Pool-Type Reactor (LPTR) was used for the irradiations. Gamma-ray spectra were taken with a 40-cm³

Table 1. Projected key chemical constituents of collected particulate matter.

Element or molecular constituent	Remarks and possible origins
C (total and organics)	Primary-natural and anthropogenic sources secondary-photochem (?)
N(NO ₃ ⁻ , NH ₄ ⁺ , amino and pyridino	Sources - oxidation of NO _x , NH ₃ , fuel additives
Na ^a	Mainly sea salt
Al ^a	Mainly soil - some possible-anthropogenic
Si	Mainly soil
S(SO ₄ ⁻ , SO ₃ ⁻ , S ^{...})	Mainly secondary production from SO ₂ oxidation
Cl ^a	Mainly sea salt, but some man made
K ^a	Mainly natural (?)
Ca ^a	Cement production
Tl ^a	Anthropogenic and natural
V ^a	Power plant - fuel oil
Cr ^a	Anthropogenic
Mn ^a	Anthropogenic
Fe ^a	Anthropogenic and natural
Ni	Anthropogenic
Cu ^a	Anthropogenic
Zn ^a	Tire dust, smelting, fuel additives
As ^a	Combustion, metal prod. and proc.
Se ^a	Combustion
Br ^a	Auto exhaust
Cd	Metal prod. and proc.
I ^a	Sea salt and (?)
Ba ^a	Diesel exhaust and lub oil atomization
Pb	Auto exhaust, industrial proc.
H ₂ O	Liquid water content is a potentially important inert ingredient in visibility question

^aElements detected by INAA.

lithium-drifted germanium detector, Ge(Li). For a complete irradiation sequence, 20 to 30 elements were reported. For a short irradiation, about 10 elements were routinely detected. The data-transmission time was as short as one day and normally one week for short-irradiation elements,

and was about a month for long-irradiation elements.

As a result of these studies, new methods of aerosol analysis using NAA are considered to be useful operational methods for samples collected over two-hour periods in urban air.

Description of Instrumental Neutron Activation Analysis (INAA)

Since its inception, INAA has become increasingly more important as a tool for doing trace-element analysis. This is due to progressive improvements in its sensitivity made possible by the use of high-resolution, solid-state radiation detectors, improved data-reduction techniques and schemes, and increased experience in sample preparation and collection methods.

To be most useful, the INAA technique requires a high thermal neutron flux of the type usually found only in a nuclear reactor. Neutron fluxes of 10^{12} to 10^{14} n/cm²/sec can be easily obtained at most reactor facilities.

BASIC PRINCIPLES

The procedure used for INAA is to take a sample, expose it to a neutron flux, measure the induced activity as a function of energy, and evaluate the data to quantify the elements present in the original samples (Fig. 1). In practice, the samples contain many elements and occasionally several isotopes of the same element. The activation/counting scheme employed must be chosen in such a manner as to optimize the activity of as many elements as is reasonably possible. This involves making two or more separate irradiations for each sample and applying various counting

Fig. 1. Schematic diagram of instrumental neutron activation analysis procedure.

schedules, depending on the type of sample and the elements being sought in the analysis. The irradiation schedule and counting scheme used in this study are discussed in detail below.

The terms Q1 and Q2 refer to the first and second count respectively, after the short irradiation, and L1, L2, L3 likewise refer to the long irradiation.

For this study the neutron source was the Livermore Pool-Type Reactor (LPTR). The LPTR is a 3-MW thermal research reactor operated for the U.S. Energy Research and Development Administration (ERDA) by the University of California Lawrence Livermore Laboratory.

Figure 2 is a block diagram of the detector system used. It is built around

Fig. 2. Block diagram of INAA detector system.

a 40-cm³ Ge(Li) detector, coupled to a 4096-channel pulse-height analyzer and the appropriate linear electronics.

IRRADIATION AND COUNTING PROCEDURE

The irradiation and counting scheme shown in Table 2 was designed to give the maximum sensitivity for the wide range of elements. The scheme is similar to that used by others for the same type of analyses.¹⁻³

The data derived were recorded on computer-compatible magnetic tape for permanent reference and for subsequent reduction and analysis. The procedure is effective for the identification of approximately 35 elements in a single sample.

Table 3 gives a listing of the parent nuclide, half-life, daughter product, and energy of the gamma rays used in the analysis of the elements of interest.

Table 3 shows that ⁶⁵Zn has a gamma ray with an energy of 1115.4 keV. Thus, if there are large amounts of both Zn and Sc in a sample, it may not be possible to separate the gamma-ray peaks since they would overlap when detectors with currently available resolutions are used. Scandium has another gamma ray with an energy of 889.4 keV, and the only appreciable interference with this peak is the ^{110m}Ag gamma ray at 884.7 keV. By the use of curve-fitting techniques and spectrum stripping, it is possible to resolve large amounts of ^{110m}Ag, ⁴⁶Sc, and ⁶⁵Zn in the same sample. A close examination of Table 3 reveals several other interferences of the type discussed above which occur in a typical sample. The detection limits for 75 elements are given in Table 4, based on a maximum irradiation time of one hour, a thermal neutron flux of 10¹³ n/cm²/sec, and no appreciable interferences.⁴ These detection limits can,

Table 2. Neutron-irradiation and sample-counting schedule.

Irradiation time, flux	Cooling time	Counting time	Elements detected
2 min 2 × 10 ¹³ n/cm ² /sec	4 min	500 sec (Q1)	Al, V, Cu, Ti, Ca
	20 min	1000 sec (Q2)	Na, Mg, Cl, Mn, Br, I, Ba, Ir
12 hr 5.1 × 10 ¹² n/cm ² /sec	20-30 hr	40 min (L1)	Eu, Br, As, W, Ga, Zn, K, Cu, Na, Cd
	6-10 days	80 min (L2)	Sm, Au, Hg, La, Sb
	20-30 days	600-800 min (L3)	Fe, Cr, Co, Zn, Hg, Se, Ag, Sb, Ce, Eu, Sc, Th, Ni, Ta, Hf, Ba, Rb, Zr, Cs, Yb, Tb, Lu

Table 3. Parent, daughter, half-life, and energy of observed gamma rays for elements analyzed by INAA technique in this study.

Parent element exposed	Daughter isotope observed	Half-life ^a	Gamma-ray energy observed ^b
Ti	⁵¹ ₂₂ Ti	5.79 m	320.0(100)
Mg	²⁷ ₁₂ Mg	9.46 m	843.8(100), 1014.5(37.5)
Cu	⁶⁶ ₂₉ Cu	5.10 m	1039.2(100)
V	⁵² ₂₃ V	3.75 m	1434.3(100)
Al	²⁸ ₁₃ Al	2.32 m	1778.7(100)
Ca	⁴⁹ ₂₀ Ca	8.80 m	3084.4(100)
Ba	¹³⁹ ₅₆ Ba	82.9 m	165.8(100)
I	¹²⁸ ₅₃ I	25.0 m	443.3(100), 526.4(9.9)
Br	⁸⁰ ₃₅ Br	16.8 m	616.2(100), 665.6(17.2)
In	¹¹⁶ ₄₉ In	53.7 m	417.0(40.2), 1097.1(59.8), 1293.4(100)
Na	²⁴ ₁₁ Na	15.0 h	1368.4(100), 2754.1(100)
Cl	³⁸ ₁₇ Cl	37.3 m	1642.7(74.5), 2167.6(100)
Mn	⁵⁶ ₂₅ Mn	155.0 m	846.7(100), 1811.2(29.4)
As	⁷⁶ ₃₃ As	26.4 h	559.1(100), 657.1(100)
W	¹⁸⁷ ₇₄ W	23.9 h	134.2(31.6), 479.5(83.1), 618.2(23.1), 685.7(100)
Ga	⁷² ₃₁ Ga	14.1 h	629.9(25.5), 834.0(100), 2201.6(27.3)
K	⁴² ₁₉ K	12.4 h	1524.7(100)
Cd	¹¹⁵ ₄₈ Cd	53.5 h	452.3(29.5), 527.9(100)
Sm	¹³³ ₆₂ Sm	48.8 h	103.2(100)
Au	¹⁹⁹ ₇₉ Au	64.7 h	411.8(100)
La	¹⁴⁰ ₅₇ La	40.2 h	328.8(21.4), 487.0(49.4), 1596.6(100)
Fe	⁵⁹ ₂₆ Fe	45.6 d	1099.3(100), 1291.5(77.0)

Table 3. (continued)

Parent element exposed	Daughter isotope observed	Half-life ^a	Gamma-ray energy observed ^b
Cr	⁵¹ ₂₄ Cr	27.8 d	320.1(100)
Co	⁶⁰ ₂₇ Co	5.26 y	1173.2(100), 1332.5(100)
Zn	⁶⁵ ₃₀ Zn	24.3 d	1115.5(100)
Hg	²⁰³ ₈₀ Hg	46.9 d	279.2(100)
Sc	⁷⁵ ₃₄ Sc	120 d	136.0(86.0), 264.7(100)
Ag	^{108m} ₄₇ Ag	5.00 d	434.0(100), 614.4(100), 723.0(100)
Ag	^{110m} ₄₇ Ag	255 d	657.7(100), 884.7(79.6), 937.5(36.5), 1384.2(27.7)
Sb	¹²⁴ ₅₁ Sb	60.3 d	602.7(100), 1691.1(53.2)
Ce	¹⁴¹ ₅₈ Ce	32.5 d	145.5(100)
Eu	¹⁵² ₆₃ Eu	12.7 y	121.8(100), 344.2(85.6), 1408.1(65.0)
Sc	⁴⁶ ₂₁ Sc	83.9 d	889.3(100), 1120.5(100)
Th	²³³ ₉₁ Pa	27.0 d	311.9(100)
Ni	⁵⁸ ₂₇ Co	71.3 d	811.1(100)
Hf	¹⁷⁵ ₇₂ Hf	70.0 d	343.4(100)
Hf	¹⁸¹ ₇₂ Hf	42.5 d	133.1(49.4), 482.2(100)

^aTime units are as follows: m = minutes, h = hours, d = days, y = years.

^bNumbers given in parentheses following the gamma-ray energy are the relative intensities (%) of the gamma rays.

therefore, be thought of as theoretical limits within the state of the art. Detection limits are shown in Table 5 for the two-hour samples analyzed in the ACHEX study.

STANDARDIZATION

In order to generate accurate quantitative information, neutron activation

analysis (NAA) must make accurate comparisons of the sample elemental counting information with that for the elemental standard. The elemental standards are individually prepared by dissolving a known amount of the element of interest as a high-purity metal, oxide or assayed compound, as the chemistry dictates, into triple-quartz-distilled water or

dilute quartz-distilled acid. Aliquots of these standards are then spotted onto blank filters of Whatman 41 or Gelman GA-1, and the filters are processed through the routine NAA procedure described above. These experiments basically provide values of the conversion factor of nanograms per count for each

Table 4. Detection limits (theoretical) of INAA technique for 75 elements, assuming a 1-hr irradiation with a thermal neutron flux of 10^{13} n/cm²/sec and no appreciable interferences.

Limit of detection (μg)	Elements
$1-3 \times 10^{-7}$	Dy
$4-9 \times 10^{-7}$	Eu
$1-3 \times 10^{-6}$	-
$4-9 \times 10^{-6}$	Mn, In, Lu
$1-3 \times 10^{-5}$	Co, Rh, Ir
$4-9 \times 10^{-5}$	Br, Sm, Ho, Re, Au
$1-3 \times 10^{-4}$	Ar, V, Cu, Ga, As, Pd, Ag, I, Pr, W
$4-9 \times 10^{-4}$	Na, Ge, Sr, Nb, Sb, Cs, La, Er, Yb, U
$1-3 \times 10^{-3}$	Al, Cl, K, Sc, Se, Kr, Y, Ru, Gd, Tm, Hg
$4-9 \times 10^{-3}$	Si, Ni, Rb, Cd, Te, Ba, Tb, Hf, Ta, Os, Pt, Th
$1-3 \times 10^{-2}$	P, Ti, Zn, Mo, Sn, Xe, Ce, Nd
$4-9 \times 10^{-2}$	Mg, Ca, Tl, Bi
$1-3 \times 10^{-1}$	F, Cr, Zr
$4-9 \times 10^{-1}$	Ne
1-3	S, Pb
4-9	Fe

Table 5. Limits of detection^a for trace elements in aerosols with instrumental neutron activation (ng/m³).

Element	Gelman GA-1	Impactor filter ^b
Na	300	200
Mg	100	10
Al	0.3	100
Cl	1	1
Ca	1	10
Ti	10	1
V		0.1
Mn	0.6	
Cu	0.1	1
Br		0.0003
In	0.002	0.0004
I		.02
Ba	2	0.5

^aAbove blank.

^bAverage results for 0.0006-cm Mylar, 0.0025-cm Teflon, and 0.0025-cm polyethylene covered with 0.004-cm sticky resin.

element which is then applied to the sample count data by a computer code to calculate the elemental weights on the filters and impactor surfaces.

The standardization methods differ for short and long irradiations. The main similarity in the two methods is that both are pre-mixed solutions containing only those elements of interest. Both have the shortcoming of having to prepare standards of approximately the same concentrations as the samples of interest. This necessitates an estimation of the composition of the sample. This estimation is critical if one is looking at samples which contain large amounts of elements that have interfering gamma rays such as silver, scandium and zinc, as described above, and if any

of the short-lived isotopes (eq., Al, V, Ti) vastly predominate during the Q1 count.

For short irradiations, all samples are normalized to a "standard flux monitor." Several different types of flux monitors have been used by different investigators depending on their specific applications, but each was designed to do the same thing, namely, to normalize a given irradiation back to some known condition or parameter. For this study, a titanium flux monitor was used and counted for 60 seconds between the Q1 and Q2 counts. Several titanium flux monitors were in use, and all were run for a predetermined time and counted and found to be statistically identical. The flux monitors were placed in the same position with respect to the sample in the sample carrier during each irradiation. The counts from the flux standard were then ratioed to the master standard count taken with the same flux monitor, and all elemental counts were then ratioed up or down by the same factor. The ratioing was performed by the data reduction program, and the program "flags" any standard ratio that deviates from the master standard by more than 10%.

For the long irradiations, a standard was prepared for each irradiation. The standard was then irradiated with and counted in the same position and sequence as the sample. Any flux variation that existed from one irradiation to another was thereby taken into account. This procedure effectively calibrated the detector for each sample run.

DATA REDUCTION

The data reduction for the INAA portion of this study was performed

using the gamma-ray analysis program MIKEGAM. This program is an adapted version of a technique developed by Ralston and Wilcox.⁵ The accuracy of the code has been verified by use of interlaboratory and intralaboratory comparison studies, which are discussed below.

Basically, the code operates by generating a baseline from the Ge(Li) spectrum, and from this baseline defining and quantitating significant peaks. The program has two major branches; one for processing short irradiation samples, and the other for processing long irradiation samples. The errors contributed by counting statistics, sampling, blank contribution and standards determination are carried along and combined in the final calculations.

SPECIMEN HANDLING PROCEDURE

Our procedures were planned for the following types of samples: GA-1 filters, 0.25- by 1-inch strips of Mylar, and 1-in.-diam Whatman 41 Hi-Vols, sticky film, and paraffinated Mylar. All samples were handled with blunt-ended stainless steel tweezers and inserted into 2-dram polyethylene vials which had been previously cleaned. A vial was then loaded into a reactor polyethylene pneumatic tube "rabbit" along with a titanium foil flux monitor (encased in polyethylene) and a polystyrene disc which acted as a shock absorber. After irradiation, the sample was removed from the inner vial after the outer "rabbit" had been discarded and the sample was inserted into a clean cellophane bag using clean stainless steel tweezers. The bag-encased sample was then inserted into a Lucite sample holder and placed in

front of a Ge(Li) detector for gamma-ray counting (re. counts Q1 and Q2). For samples undergoing the long irradiation procedure, a decay period of at least three days was allowed before the long irradiation to allow any radioactivities generated in the short irradiation to die away. For the long irradiation, approximately 12 samples were individually bagged in clean polyethylene, and along with bagged elemental standards, were loaded into a polyethylene capsule which rotated during the 12-hour irradiation to insure flux homogeneity. After the irradiation, the samples were run through the L1, L2, and L3 counts. Particular care was taken not to introduce any contaminants in the samples during

the short irradiation and subsequent analysis so that the long irradiation analysis would not be affected.

DETERMINATION OF PROCEDURAL ERRORS

To determine the overall error contributed by various procedures such as weighing and pipetting, and also the geometry in the reactor irradiation facility and the gamma spectrometer, six sodium standards were prepared in the usual manner, irradiated together, and then counted sequentially. The overall variation in obtained activity from each sodium standard showed a fractional standard deviation of less than 1%.

Results

BLANKS

The assignment of average trace quantities in the filter substrate (blank) ranked high among the various factors that had an effect on the precision of trace element analysis by INAA of air particulate matter collected on filter media. This was especially true when a trace element in the blank was determined with a high degree of uncertainty and the concentration of the deposited trace element approached that contained in the blank.

For Phase I, various particle collection media were studied. Initially, the effort was directed toward the evaluation of candidate substrates and after final selection to a more detailed characterization of those chosen. The major candidates were Gelman (GA-1), Millipore, a sticky-surface polyethylene film, Mylar, Teflon film,

and paraffinated Mylar. An additional variable was the pre-treatment of the media which consisted of washing either by the factory or by AIHL.

Phase II sample collection was restricted to the use of GA-1 filters for the total and after filters, sticky polyethylene film for the Lundgren impactor surfaces, and W-41 for the high-volume samples. Phase I blank values for W-41 and sticky polyethylene were used, but since a new washing procedure was used on Phase II GA-1 filters, a separate study was done for them.

Table 6 shows the trace element values in nanograms per square centimeter for each of the substrates used in Phases I and II. The values shown are the grand averages of a varying number of samples of each substrate. They, along with the associated probable errors shown in parentheses, are the best determination of a single value

Table 6. Grand averages of sample substrate blank determinations (ng/cm²).

	Phase II GA-1	Phase I GA-1	Mylar	Teflon	Sticky film	Parafin mylar	W-41
Na	53 (0.50)	88.8 (0.2)	2.8 (0.2)	1.5 (0.2)	206 (0.08)	25.01 (0.08)	94.2 (0.17)
Mg	92 (0.24)	ND	ND	ND	ND	ND	ND
Al	41 (0.45)	29.6 (0.2)	4.0 (0.2)	4.45 (0.2)	17.5 (0.43)	67.4 (0.04)	21.5 (0.20)
Cl	158 0.21	178 0.2	6.8 0.2	2.6 0.2	86.4 0.14	34.5 0.12	407 0.20
Ca	176 (0.41)	158 (0.2)	ND 0	ND 0	285 (0.30)	57.7 (0.83)	70 (0.20)
Sc	0 3	ND ND	ND ND	ND ND	ND ND	0 0	0.01 (0.12)
Ti	ND ND	ND ND	ND ND	3.30 (0.20)	3.82 (0.52)	5.89 (0.52)	ND ND
V	ND ND	ND ND	ND ND	0.016 (0.20)	0.0272 (0.29)	0.112 (0.26)	ND ND
Cr	0.99 (0.11)	8.0 (0.28)	0 0	1.85 (0.03)	0.55 (0.12)	0 0	1.46 (0.04)
Mn	0.82 0.74	0.53 0.2	0.03 0.2	0.44 0.2	0.443 0.53	0.722 0.28	0.42 0.20
Fe	29.4 (0.27)	56 (0.3)	ND 0	11 (0.44)	80 (0.08)	ND ND	25.8 (0.09)
Co	ND ND	ND ND	ND ND	2.26 (0.03)	ND ND	ND ND	0.21 (0.03)
Cu	16 (0.41)	15.8 (0.20)	ND ND	1.90 (0.20)	3.85 (0.55)	ND ND	13.4 (0.16)
Zn	4.5 (0.15)	ND ND	31.8 (0.07)	1.5 (0.2)	300 (0.01)	ND ND	4.51 (0.09)
Ga	ND ND	ND ND	0.005 (0.005)	0.36 (0.36)	0.10 (0.10)	ND ND	ND ND
As	ND ND	ND ND	0.005 (0.005)	0.36 (0.36)	0.10 (0.10)	ND ND	ND ND
Br	0.38 (0.36)	ND ND	0.44 (0.20)	ND ND	0.85 (0.21)	2.26 (0.03)	13.8 (0.95)
Cd	ND ND	ND ND	0.005 (0.005)	0.36 (0.36)	0.10 (0.10)	ND ND	0.075 (0.32)
Sb	ND ND	ND ND	114 (0.905)	0.02 (0.36)	0.15 (0.10)	ND ND	0.034 (0.12)

Table 6. (continued)

	Phase II GA-1	Phase I GA-1	Mylar	Teflon	Sticky film	Parafin mylar	W-41
I	0.36 (0.10)	ND ND	ND ND	ND ND	ND ND	0.11 (0.70)	ND ND
La	ND ND	ND ND	0.005 (0.005)	0.36 (0.36)	0.10 (0.10)	ND ND	ND ND
Ce	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	0.11 (0.18)
Hf	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	0.82 (0.10)
Au	ND ND	ND ND	ND ND	ND ND	ND ND	ND ND	2.44 (0.07)
Hg	0.39 (0.5)	12.6 (0.06)	2.6 (0.50)	1.2 (0.5)	3.0 (0.5)	ND ND	0.16 (0.30)
Th	ND ND	ND ND	ND ND	0.007 (0.35)	0 0	ND ND	0.025 (0.27)

which represents the population of filter (or impactor) media which was used in the sampling under field conditions.

The experience gained during Phase I showed that a better statistical sampling of the pool of washed GA-1 filters was in order for Phase II. Accordingly, the following studies were carried out.

Phase II, GA-1, Series 1

A representative group of 13 washed filters which had first been analyzed at LBL was analyzed with the results shown in Table 7. Of particular interest is the extreme variability in the Na values for the 13 filters, the range being an order of magnitude. The 95% confidence interval or two standard deviations is in excess of 200%. Also, Cu, V, and Br show high variability, although not as severe as that of Na.

When these blank values were used in computing the results for particulate loadings on the after and total filters, it became apparent that they were too high since detection limits were being reported where they were not expected. Comparison of these blank values to those obtained for Phase I blanks gave ratios as high as 4.5. No reasonable explanation was found for these discrepancies. It was decided to examine another representative group of blanks.

Phase II, GA-1, Series 2

Eight additional GA-1 blank filters were subjected to analysis. The results are shown in Table 8. Again, extremely high variability was seen among the Na values as well as Cu, Al, Ca, and Mn. However, the average values produced more believable results when applied to

Table 7. AIHL Phase II GA-1 lab blanks - first set (ng/cm²).

	BL0630BF4	BL0650BF4	BL0790BF4	BL0800BF4	BL0810BF4	BL0820BF4	BL0860BF4	BL0669BF4	BL0880BF4
Ti	10.9	13.2	13.7	14.7	10.5	14.9	14.0	12.7	13.7
Cu	105	61.7	45.6	51.5	45.8	38.1	56.3	29.2	24.7
Al	183	143	155	198	181	207	188	119	148
Ca	525	682	621	644	750	0.578	560	619	778
V	<0.14	<0.12	<0.25	<0.14	0.296	<0.13	0.193	0.142	0.123
I	0.365	0.294	0.682	0.472	0.779	0.813	0.387	0.817	0.919
Br	0.943	3.00	3.75	2.96	2.85	1.02	1.63	0.288	0.272
Na	127	61.7	113	145	166	597	63.9	221	300
Cl	507	444	496	479	485	419	453	438	435
Mn	3.57	1.79	2.25	1.83	1.76	1.47	2.31	1.89	3.05
Ba	<6.6	<5.7	<6.1	<6.3	<6.5	<7.2	<6.0	<6.4	<6.7
Mg	169	166	105	183	239	194	146	246	322
In	<0.009	<0.009	<0.009	0.009	<0.009	0.01	<0.009	<0.01	0.030
	BL0880BF4	BL0581BF4	BL0590BF4	BL0610BF4	X	σ	FSD		
Ti	<15.1	<13.9	<12.1	<17.7	ND	ND	ND		
Cu	103	74.2	30.2	35.9	54.0	26.2	0.49		
Al	141	155	134	264	170.5	38.7	0.23		
Ca	665	619	593	1003	669.8	119	0.18		
V	0.087	0.197	0.055	<0.17	0.156	0.781	0.52		
I	0.667	0.680	0.544	0.598	0.617	0.195	0.32		
Br	2.70	2.50	2.23	3.29	2.11	1.16	0.55		
Na	63.6	59.1	74.6	740	210	217	1.03		
Cl	485	418	390	683	472	72.4	0.15		
Mn	1.82	2.72	1.95	2.84	2.25	0.62	0.28		
Ba	<6.6	<6.0	<5.5	<6.9	ND	ND	ND		

Table 8. AIHL Phase II GA-1 lab blanks — second set (ng/cm²).

	BL0969BF	BL0979BF	BL0989BF	BL0999BF	BL1009BL	BL1019BL	BL1029BL	BL1079BL	Avg ² (ng/cm ²)	σ	FSD
Ti	< 9.0	< 7	< 8	< 7	9.25 0.82	< 9	< 9.7	< 8	ND	ND	ND
Mg	115 0.477	< 87	< 92	< 89	84	72 0.63	< 123	88.5 0.49	ND	ND	ND
Cu	13.4 0.20	9.63 0.22	22.6 0.12	12.7 0.18	18.8 0.13	26.7 0.12	11.8 0.27	9.3 0.27	15.6	6.5	0.42
V	< 0.08	< 0.06	< 0.07	< 0.06	< 0.06	< 0.08	< 0.09	< 0.07	ND	ND	ND
Al	64.7 0.046	31.2 0.055	32.5 0.055	23.7 0.06	22.1 0.06	43.7 0.05	72.0 0.05	36.7 0.05	40.8	18.4	0.45
Ca	140 1.11	156.3 0.88	72.7 0.52	176.1 0.29	152.5 1.04	168.7 0.86	251.8 1.04	289.2 0.23	175.9	71.8	0.41
Ba	< 4.2	< 3.4	< 3.5	< 3.5	< 3.4	< 3.7	< 4.6	< 3.7	ND	ND	ND
I	< 0.28	< 0.22	< 0.22	0.30 0.37	< 0.22	< 0.23	< 0.31	0.34 0.32	ND	ND	ND
Br	< 0.82	< 0.7	< 0.7	< 0.7	0.48 0.03	< 0.72	< 0.91	0.28 0.03	ND	ND	ND
In	< 0.03	< 0.005	< 0.005	< 0.005	< 0.005	< 0.006	< 0.007	< 0.006	ND	ND	ND
Na	124.1 0.05	23.6 0.15	7.74 0.31	24.6 0.14	< 5.5	9.4 0.29	185.5 0.05	11.3 0.26	55.0	70	1.1
Cl	153.3 0.07	144.9 0.07	157.5 0.06	167.6 0.06	143.3 0.07	161.9 0.07	212.2 0.06	176.6 0.06	160	34	0.21
Mn	0.656 0.99	0.53 0.37	0.64 1.04	0.38 0.52	< 0.42	< 0.47	< 0.57	0.52 0.40	0.54	0.11	0.21

the analysis of particulate matter collected on the after and total filters. Comparison with Phase I GA-1 blanks and Phase II field blanks tends to support the validity of the blank values for this set.

Even though the expected error for individual determinations may have been rather small, the standard deviation of the eight measurements must be used in the computer program library which describes the average blank. Consequently, as the measured trace element approaches the blank value, the probable error associated with the blank begins to predominate and the reported trace element will have a large probable error associated with it.

Field Blanks

Data for 28 field blanks are presented in Table 9. Again, Na showed extremely high variability. Since these blanks were exposed to field conditions, the variability across any single element cannot necessarily be attributed solely to the innate variability of the unexposed blanks.

Table 10 is a summary of the field blank data showing means, standard deviations and fractional standard deviations. The means for the second series of laboratory blanks are included for comparison.

When the field blank mean is ratioed to the lab blank mean, all cases show values greater than unity, with Br exceptionally high (16:1). Since we are dealing with statistical sampling, inspection of these ratios cannot give a satisfactory answer to the question of whether the means are significantly different. Using the student-t test at the level of $\alpha = 0.05$ (95% confidence), it is found that all but Mn, both means for Na, Mg, and I can be said to have different means ($\mu_1 \neq \mu_2$).

Thus, we can say that to a confidence level of 0.95, something occurred to the field blanks to cause Cu, Al, Ca, Cl, and Br to be elevated relative to the laboratory blanks. This conclusion should be tempered quite a bit considering the unequal sample sizes in the lab field blanks and the relatively small number of lab blanks. If further hypothesizing is attempted, it is suggested that a separate study be done using larger sampling; or perhaps better still, using the same filters in both laboratory and field studies and analyzing the filters before and after they are subjected to field conditions.

QUALITY ASSURANCE

Bromine-Loss Test

Tests were carried out on a high-volume Whatman 41 filter run in Livermore for 24 hours during a rainy day. Two 1-inch circles were cut out of the paper and run on the LLL Radiochemistry Division isotopic-source XRFA system on the same day. The circles were then inserted into the LPTR for a 2-minute irradiation and later counted again on the XRFA system. The Br loading on the 1-inch circles is as follows:

	<u>Before (μg)</u>	<u>After (μg)</u>	<u>Difference (%)</u>
No. 1	5.09 ± 0.25	5.14 ± 0.26	$+(0.98 \pm 6.9)$
No. 2	5.45 ± 0.27	5.16 ± 0.26	$-(5.3 \pm 6.8)$

From these results we conclude that Br loss, if any, caused by a 2-minute reactor irradiation is less than 5%. We hope to carry out Br determinations with smaller errors in the near future.

Tests were also performed to compare the absolute determination of Br XRFA and NAA:

Table 9. Field blanks - Phase II, total (ng/blank).

	TA0759BF	TB0770BF	TC0782BF	TD0794BF	UF0817BF	UG0833BF	VH1049BF	VH1051BF	VH1120BF	VJ0859BF	VJ1059BF
Mg	612	< 699	< 688	< 578	< 555	609	450	< 533	< 525	< 597	< 509
Cu	91.5	123	85	67	67	197	65	68	58	152	62
Al	266	529	467	298	263	272	172	192	195	303	226
Ca	1303	1873	972	627	973	716	1098	1593	748	1730	1298
Ti	< 48	< 57	< 54	< 52	< 46	< 54	< 43	< 46	< 46	< 49	< 41
V	< 0.41	< 0.51	< 0.48	< 0.44	0.34	< 0.42	< 0.36	< 0.38	< 0.39	0.093	< 0.37
I	2.4	3.0	3.0	3.0	2.5	2.8	2.8	< 1.4	< 1.4	1.2	1.2
Br	12.6	30	33.4	23.7	14.6	31	13.3	13.4	14.6	7.3	11.8
Na ^a	257	365	689	351	386	431	94	146	64	102	46
Cl ^a	969	978	1080	1045	837	1054	876	962	1021	854	836
Mn	3.1	6.6	2.9	3.2	3.7	6.2	3.7	3.7	5.0	< 2.4	< 2.3
Ba	< 21	< 24	< 24	< 24	< 21	< 24	< 20	< 22	< 21	< 21	< 19
In	< 0.031	< 0.032	< 0.032	< 0.033	< 0.028	< 0.032	< 0.03	< 0.032	< 0.03	< 0.03	< 0.028
	WK1106BF	WL1043BF	WL1046BF	CL0855BF	FI0838BF	CK0907BF	DK0801BF	EK0928BF	FK0809BF	GK1017BF	
Mg	432	< 526	< 857	< 551	< 639	< 637	< 724	691	219	682	
Cu	54	68	71	52	37.6	113.6	245	179	204	146	
Al	167	225	484	238	400	353	530	346	344	265	
Ca	1025	1056	1658	1371	901	1379	1465	1418	1403	1738	
Ti	< 42	< 44	39	39	< 56	< 56	< 65	< 59	< 60	< 54	
V	< 0.36	< 0.39	< 0.60	< 0.40	0.52	< 0.047	0.79	0.912	0.347	0.62	
I	2.7	5.7	8.2	3.0	2.7	1.9	4.1	3.6	3.3	2.4	

Table 9. (continued).

Br	13.4	13.2	27	45	51	44	54	63	59	42
Na ^a	145	138	2297	348	332	151	252	294	231	105
Cl ^a	896	901	2149	923	974	1033	1220	1161	1226	1006
Mn	3.2	< 2.5	6.1	5.8	6.1	6.1	8.4	6.8	7.3	4.2
Ba	< 20	< 21	< 34	< 24	< 26	< 25	< 28	< 28	< 28	< 24
In	< 0.032	< 0.029	< 0.05	< 0.032	< 0.034	< 0.032	< 0.038	< 0.035	< 0.036	< 0.036

	CF0697BF	DF0708BF	CE0615BF	DE0571BF	EE0552BF	FF0626BF	GE0561BF	$\bar{X}$	σ	FSD
Mg	< 628	< 805	< 693	< 566	< 716	1014	715	603	222	0.37
Cu	132	96	171	104	105	143	53	107.5	54	0.50
Al	312	592	408	145	503	420	359	331	124	0.37
Ca	1428	1123	1652	657	1386	1067	1107	1260	365	0.29
Ti	67	< 66	< 60	< 47	< 59	< 57	< 54	ND	ND	ND
V	< 0.45	0.44	< 0.50	0.42	0.56	0.51	< 0.47	0.505	0.222	0.49
I	3.0	4.6	2.2	2.1	2.8	3.6	2.6	3.1	1.4	0.41
Br	40	37	37	28	35	34	37	30.9	15.6	0.50
Na ^a	247	1086	787	346	539	285	763	402 ^a	445	1.1
Cl ^a	1194	1487	1362	1277	1214	1256	1192	304 ^a	204	0.67
								1106	265	0.23
								1051 ^a	153	0.15
Mn	7.4	8.9	3.2	4.7	5.7	5.2	4.2	5.3	1.7	0.32
Ba	< 25	< 29	28	< 25	< 25	< 25	< 26	ND	ND	ND
In	< 0.033	0.041	0.039	< 0.036	< 0.037	< 0.036	< 0.036	ND	ND	ND

^a $\bar{X}$ and σ were calculated twice, the first time using all values and the second time omitting the two highest values.

Table 10. Field blank summary - Phase II.

	Avg (ng)	σ	FSD	Avg (ng/cm ²)	GA-1 Phase II lab blank avg (ng/cm ²)	Field blank/ lab blank	By t-Test, H ₀ : $\mu_1 = \mu_2$ at $\alpha = 0.05$
Mg	603	222	0.37	119	92 ^c	1.3	$\mu_1 = \mu_2$
Cu	108	54	0.50	21.3	16	1.3	$\mu_1 \neq \mu_2$
Al	331	124	0.37	65	41	1.6	$\mu_1 \neq \mu_2$
Ca	1260	365	0.29	24 ^o	176	1.4	$\mu_1 \neq \mu_2$
Ti	ND	ND	ND	ND	ND	ND	
V	0.51	0.22	0.43	0.10	ND	ND	
I	3.1	1.4	0.45	0.61	0.32 ^c	1.91	$\mu_1 = \mu_2$
Br	31	16	0.52	6.1	0.38 ^c	16.1	$\mu_1 \neq \mu_2$
Na ^a	402	445	1.11	79.3	55	1.4	$\mu_1 = \mu_2$
Na ^b	304	204	0.67	60	55	1.1	$\mu_1 = \mu_2$
Cl ^a	1106	265	0.24	218	158	1.4	$\mu_1 \neq \mu_2$
Cl ^b	1051	153	15	207	158	1.3	$\mu_1 \neq \mu_2$
Mn	5.3	1.7	0.32	1.04	0.82	1.3	$\mu_1 = \mu_2$
Ba	ND	ND	ND	ND	ND	ND	
In	ND	ND	ND	ND	ND	ND	

^aIncludes all values.^bExcludes two highest values.^cThese values were derived by averaging those out of eight filters which had detectable Bromine, Iodine, or Magnesium.

	<u>XRFA (μg)</u>	<u>NAA (μg)</u>	<u>Difference (%)</u>	between the LBL XRFA results and the LLL NAA results for Br was reasonable within the error limits: ⁶
No. 3	5.42 $\pm$ 0.27	5.81 $\pm$ 0.29	6.7 $\pm$ 6.0	
No. 4	5.39 $\pm$ 0.27	6.03 $\pm$ 0.30	10.6 $\pm$ 6.6	

These results seem to indicate a slight discrepancy between the LLL NAA and XRFA analyses. However, to be able to reach a definite conclusion, more accurate tests must be conducted. Interlaboratory comparisons on high-volume Whatman 41's in Phase I demonstrated that the agreement

	<u>Difference (%)</u> <u>(NAA - XRFA)</u>
Riverside	+17 $\pm$ 14
Pasadena	+17 $\pm$ 16
Fresno	+12 $\pm$ 11
Bakersfield	-14 $\pm$ 11
Berkeley (AA0006)	-14 $\pm$ 10
Berkeley (AA0007)	+10 $\pm$ 11

Additional tests were also run to determine H₂O loss upon standing and upon storage in an evacuated desiccator. Whatman filters were allowed to stand for one week open to room atmosphere and temperature and in an evacuated desiccator. No loss was observed in either experiment.

Nitrate Losses

During some nitrate validation studies in ACHEX, a question was raised as to the volatile loss of nitrate during INAA. Samples are subjected to moderate heating (135°F), to gamma and neutron irradiation during NAA, all of which might cause nitrate loss.

To assess directly the importance of nitrate loss under NAA condition, three filter samples collected during the 1972 sampling period (ACHEX-1) in Riverside, were split in half, and one piece was subjected to NAA. The pieces were then analyzed for nitrate with the results as follows:

Sample	NO ₃ ⁻ /NO ₃ ⁻ (after NAA)
1	1.02
2	0.89
3	0.78

Clearly these results fail to reveal a significant loss of nitrate by exposure to NAA conditions. However, the samples available for this study had been maintained (in closed Millipore filter boxes) at room temperature for nearly two years which may have made them inappropriate for this study.

VALIDATION

For the determination of the overall accuracy of the use of INAA for the

aerosol characterization study, we had access to three different types of verification. The first of these verifications was to analyze some standard material and compare our measured values to those certified by the agency issuing the standard. In our case, we analyzed orchard leaves as certified by the National Bureau of Standards.

The second approach was to participate in an interlaboratory comparison of trace element determinations on various standardized samples. This was done for coal dust and fly ash in one series, and for gravimetric standard solutions in another.

Finally, and perhaps of major interest, was the possibility of intercomparison within the experimental program. This involves direct comparison of elements determined in the same sample by different analytical techniques and comparison of an overall view of data produced by different techniques, not necessarily looking at the same elements.

NBS Orchard Leaves (SRM-1571)

Samples of NBS standard reference material - orchard leaves - were analyzed. The values shown in Table 11 are averages of three to five replicates. The NBS certified values are also given. The values in parentheses are for informational value only and are not certified. The experimental errors are equal to two standard deviations or one-half the range of the data, whichever is greater.

NBS-EPA-Intercomparison Study of Coal Dust (SRM 1632) and Fly Ash (SRM 1633)

A "round-robin" intercomparison study was sponsored jointly by the National

Table 11. National Bureau of Standards
SRM-1571 orchard leaves
($\mu\text{g/g}$).

	LLL	NBS
Al	341 $\pm$ 39	(350)
Ca	20400 $\pm$ 1000	20900 $\pm$ 300
Ba	42.7 $\pm$ 4.7	
Mg	6600 $\pm$ 500	6200 $\pm$ 200
Br	13.0 $\pm$ 2.6	(10)
V	0.675 $\pm$ 0.029	
In	0.17 $\pm$ 0.05	
Na	89 $\pm$ 9	82 $\pm$ 6
Fe	330 $\pm$ 40	300 $\pm$ 20
Cl	635 $\pm$ 47	(700)
Mn	95 $\pm$ 3	91 $\pm$ 4
As	8.8 $\pm$ 3.4	14 $\pm$ 2
K	12200 $\pm$ 3600	14700 $\pm$ 300

Bureau of Standards and the Environmental Protection Agency. The standards were coal dust, fly ash, gasoline, and fuel oil. LLL participated in the measurements of coal dust and fly ash. Our report is reproduced herein, together with the determinations of other laboratories. We also indicate the values which have been certified by NBS. These data have been presented⁷ and are published.⁸ The results of the determinations are given in Tables 12, 13, and 14. The errors indicated are derived from the dispersion of the separately determined replicates. The absolute values of errors represent either one-half the range or two standard deviations, whichever is the larger.

Table 12 shows average values of all the elements which were determined, including those requested by NBS.

Tables 13 and 14 show the measurements on individual samples, together with the total error for that particular measure-

Table 12. LLL results for NBS/EPA
standards coal and fly ash
done by INAA (average values).

Element	SRM-1632	SRM-1633
	Coal (ppm)	Fly ash
Al	20000 $\pm$ 1130	123000 $\pm$ 6320
As	5.04 $\pm$ 0.66	51.7 $\pm$ 3.3
Ba	327 $\pm$ 19	2610 $\pm$ 170
Br	18.6 $\pm$ 2.4	ND
Ca	4220 $\pm$ 670	44800 $\pm$ 2600
Ce	18.5 $\pm$ 0.65	135 $\pm$ 7
Cl	758 $\pm$ 62	ND
Co	6.04 $\pm$ 0.29	42.0 $\pm$ 1.9
Cr	19.3 $\pm$ 0.97	126 $\pm$ 10
Eu	0.321 $\pm$ 0.011	2.22 $\pm$ 0.20
Fe	8180 $\pm$ 370	58000 $\pm$ 3030
Hf	0.724 $\pm$ 0.060	5.79 $\pm$ 0.38
In	0.196 $\pm$ 0.0120	0.321 $\pm$ 0.100
K	2260 $\pm$ 76	13840 $\pm$ 640
La	9.10 $\pm$ 0.38	65.0 $\pm$ 6.6
Mn	47.6 $\pm$ 3.4	506 $\pm$ 23
Na	313 $\pm$ 22	2800 $\pm$ 210
Sb	4.1 $\pm$ 5.3	6.38 $\pm$ 0.41
Sc	3.94 $\pm$ 0.19	28.0 $\pm$ 1.7
Sm	1.48 $\pm$ 0.07	11.1 $\pm$ 0.7
Th	2.97 $\pm$ 0.17	23.3 $\pm$ 1.3
Ti	1060 $\pm$ 120	7220 $\pm$ 670
V	38.3 $\pm$ 3.3	244 $\pm$ 24
W	0.62 $\pm$ 0.27	3.5 $\pm$ 1.1

ment. This error is given as one standard deviation and includes procedural errors and errors associated with peak area determination.

Tables 15 and 16 show the results reported by other laboratories and LLL.

Interlaboratory Comparison of Standard Samples

A comparison of trace element concentrations determined by five different

Table 13. LLL results for NBS/EPA standard coal (SRM-1632) done by INAA.

	Replicate 1 (ppm)	Replicate 2 (ppm)	Replicate 3 (ppm)	Replicate 4 (ppm)	Replicate 5 (ppm)
Al	19200 ± 550	20500 ± 580	20600 ± 590	19900 ± 580	19900 ± 570
As	4.85 ± 0.42	4.74 ± 0.37	4.95 ± 0.38	5.45 ± 0.42	5.23 ± 0.40
Ba	312 ± 18	335 ± 20	331 ± 19	322 ± 19	333 ± 20
Br	18.7 ± 2.9	17.2 ± 2.8	17.6 ± 2.8	20.1 ± 3.2	19.3 ± 2.3
Ca	4350 ± 370	4640 ± 406	4180 ± 370	3720 ± 340	4220 ± 380
Ce	18.6 ± 0.3	18.2 ± 0.3	18.2 ± 0.3	19.0 ± 0.2	18.6 ± 0.3
Cl	724 ± 29	791 ± 30	806 ± 32	756 ± 30	762 ± 30
Co	6.08 ± 0.09	5.83 ± 0.08	5.96 ± 0.09	6.17 ± 0.08	6.17 ± 0.10
Cr	19.1 ± 0.3	18.7 ± 0.4	19.1 ± 0.3	20.0 ± 0.3	19.4 ± 0.5
Eu	0.324 ± 0.008	0.321 ± 0.007	0.318 ± 0.007	0.329 ± 0.007	0.315 ± 0.008
Fe	8110 ± 160	7940 ± 160	8120 ± 170	8380 ± 170	8350 ± 180
Hf	0.682 ± 0.120	0.713 ± 0.125	0.748 ± 0.131	0.721 ± 0.125	0.757 ± 0.135
In	0.172 ± 0.015	0.215 ± 0.013	0.266 ± 0.014	0.107 ± 0.010	0.219 ± 0.012
K	2230 ± 230	2240 ± 210	2250 ± 240	2240 ± 210	2320 ± 230
La	9.41 ± 0.68	9.03 ± 0.66	8.99 ± 0.67	9.12 ± 0.68	8.93 ± 0.67
Mn	45.7 ± 1.5	50.2 ± 1.6	47.6 ± 1.6	46.7 ± 1.5	47.7 ± 1.5
Na	298 ± 13	304 ± 14	322 ± 14	322 ± 14	317 ± 14
Sb	0.847 ± 0.041	7.03 ± 0.14	1.93 ± 0.06	4.61 ± 0.08	6.24 ± 0.06
Sc	3.85 ± 0.04	3.98 ± 0.04	3.88 ± 0.04	4.09 ± 0.04	3.99 ± 0.04
Sm	1.46 ± 0.37	1.45 ± 0.38	1.46 ± 0.37	1.46 ± 0.38	1.54 ± 0.40
Th	2.90 ± 0.06	2.89 ± 0.06	2.93 ± 0.06	3.06 ± 0.06	3.05 ± 0.07
Ti	1030 ± 70	1070 ± 80	1030 ± 80	1010 ± 70	1160 ± 80
V	35.9 ± 1.6	40.4 ± 1.8	38.9 ± 1.7	38.1 ± 1.7	38.0 ± 1.7
W	0.799 ± 0.182	0.563 ± 0.150	0.716 ± 0.209	0.548 ± 0.208	0.462 ± 0.198

nondispersive x-ray fluorescence techniques used at eleven different laboratories was recently carried out.⁹ Standard samples were prepared by Columbia Scientific Industries. The INAA program at LLL and the radioactive, source-excited, nondispersive x-ray fluorescence technique used at LLL were included. Our results, compared with those reported by other investigators, are shown in line 4 of Table 17.

Each set of data reported in Table 17 consisted of our dried solution deposits and two blanks. The filter substrates were Whatman 41 and Millipore SMWP filters. The eight elements deposited on each sample were Al, K, V, Mn, Fe, Cu, As, and Pb in amount ranging from 1.7 µg/cm² to 54 µg/cm². All investigators received separate sets of standards. LLL used the same set for x-ray analysis prior to INAA.

Table 14. LLL results for NBS/EPA standard fly ash (SiM-1633) done by INAA.

	Replicate 1 (ppm)	Replicate 2 (ppm)	Replicate 3 (ppm)	Replicate 4 (ppm)	Replicate 5 (ppm)
Al	125000 ± 3000	126000 ± 3000	121000 ± 2960	118000 ± 2800	124000 ± 3000
As	51.4 ± 3.0	53.3 ± 4.1	52.3 ± 3.0	52.0 ± 3.0	49.4 ± 3.7
Ba	2700 ± 160	2590 ± 180	2680 ± 180	2610 ± 180	2480 ± 170
Ca	45600 ± 2900	45500 ± 2800	43500 ± 2700	46200 ± 2900	43300 ± 2800
Ce	136.1 ± 1.7	140.4 ± 1.8	132.5 ± 1.7	131.5 ± 1.7	133.7 ± 1.7
Co	43.0 ± 0.5	43.1 ± 0.5	41.5 ± 0.5	41.4 ± 0.5	41.1 ± 0.5
Ch	129.3 ± 1.7	132.5 ± 1.7	121.3 ± 1.6	121.0 ± 1.9	125.6 ± 1.7
Eu	2.36 ± 0.05	2.29 ± 0.05	2.17 ± 0.05	2.14 ± 0.05	2.15 ± 0.05
Fe	59600 ± 1200	59600 ± 1200	56800 ± 1200	57100 ± 1200	56700 ± 1100
Hf	6.03 ± 1.05	5.91 ± 1.02	5.65 ± 0.98	5.56 ± 0.97	5.80 ± 1.01
In	0.380 ± 0.048	0.346 ± 0.047	0.315 ± 0.044	0.326 ± 0.043	0.239 ± 0.043
K	13800 ± 1500	14200 ± 1200	13700 ± 1200	14100 ± 1200	13400 ± 1900
La	67.5 ± 4.9	68.4 ± 4.9	64.9 ± 4.8	64.0 ± 4.7	60.0 ± 4.3
Mn	520 ± 14	515 ± 14	494 ± 13	496 ± 13	506 ± 14
Na	2800 ± 110	2880 ± 110	2860 ± 110	2620 ± 100	2840 ± 110
Sb	6.49 ± 0.16	6.63 ± 0.16	6.40 ± 0.16	6.09 ± 0.20	6.32 ± 0.16
Sc	28.8 ± 0.3	29.0 ± 0.3	27.5 ± 0.3	27.3 ± 0.3	27.2 ± 0.3
Sm	11.2 ± 2.8	11.4 ± 2.9	11.2 ± 2.9	11.1 ± 2.8	10.5 ± 2.6
Th	24.1 ± 0.4	24.0 ± 0.4	23.0 ± 0.4	22.8 ± 0.4	22.8 ± 0.4
Ti	7590 ± 640	8950 ± 600	7100 ± 600	6880 ± 590	7550 ± 620
V	261 ± 14	243 ± 12	231 ± 12	236 ± 12	250 ± 13
W	4.09 ± 1.14	3.05 ± 0.93	4.22 ± 0.91	3.16 ± 1.23	3.15 ± 0.86

The gravimetric standard solutions deposited on Whatman 41 are referred to as "A" and "C." The values shown for each element in Table 17 are ratios of Whatman 41 and Millipore filter averages to the amount of gravimetric standard solution deposited. Each participant knew only which elements were deposited, not how much. The numbers in parentheses are the standard deviations reported by the various participants.

Intercomparison Within the ACHEX Program

INAA and XRFA Comparisons

A number of impactors and filters were subjected to analysis by both INAA at LLL and XRF at LBL.¹⁰ Table 18 lists a series of high-volume specimens showing comparisons for the four elements which were determined by both techniques. These are Ca, Ti, Mn and Br. It will be noted that two determinations

Table 15. NBS-EPA coal - fly ash comparison (fly ash $\mu\text{g/g}$, unless indicated).

	U. of Md.	NBS ^a	Battelle N.W.	Livermore	Washington State	Oak Ridge
Na	0.34% $\pm$ 0.03%		0.37% $\pm$ 0.02%	0.28% $\pm$ 0.02%		0.34%
K				1.38% $\pm$ 0.06%		2.54%
Ca	4.2% $\pm$ 0.5%			4.48% $\pm$ 0.26%		2.94%
Ba	0.27% $\pm$ 0.03%		0.34 $\pm$ 0.04	0.26% $\pm$ 0.02%		0.276%
Al	15.8% $\pm$ 1.2%		12.6% $\pm$ 0.4%	12.3% $\pm$ 0.6%		8.74%
Sc	27 $\pm$ 1.5		27 $\pm$ 1.0	28.0 $\pm$ 1.7		35.1
Ti	0.73% $\pm$ 0.04%		0.76 $\pm$ 0.0	0.72 $\pm$ 0.07		0.588%
V	251 $\pm$ 26	214 $\pm$ 8	220 $\pm$ 15	244 $\pm$ 24	223.6 $\pm$ 12.3	170
Cr	130 $\pm$ 5	131 $\pm$ 2	131 $\pm$ 8	126 $\pm$ 10	126.2 $\pm$ 4.3	
Mn	509 $\pm$ 15	493 $\pm$ 7	489 $\pm$ 11	506 $\pm$ 23	480 $\pm$ 10.1	441
Fe	5.2% $\pm$ 0.3%		6.51% $\pm$ 0.31%	5.8% $\pm$ 0.3%		
Co	41.2 $\pm$ 1.0	38 ^b	40 $\pm$ 2	42 $\pm$ 1.9		
As	59.6 $\pm$ 1.0	61 $\pm$ 6		51.7 $\pm$ 5.3	78.7 $\pm$ 3.6	
Sb	7.8 $\pm$ 1.5		7.2 $\pm$ 0.8	6.38 $\pm$ 0.41		7.84 $\pm$
In				0.32 $\pm$ 0.10		
Hf	7.9 $\pm$ 0.6		8.2 $\pm$ 0.8	5.79 $\pm$ 0.38		
Ta	1.64 $\pm$ 0.12		3.5 $\pm$ 0.3			
W				3.5 $\pm$ 1.1		
La	82 $\pm$ 5		82 $\pm$ 4	65.0 $\pm$ 6.6		82.1
Ce	156 $\pm$ 12			135 $\pm$ 7		
Sm	13.8 $\pm$ 0.6		12.4 $\pm$ 0.5	11.1 $\pm$ 0.7		
Eu	2.9 $\pm$ 0.2		2.3 $\pm$ 0.1	2.22 $\pm$ 0.20		
Th	23.5 $\pm$ 2.0	24 ^b	26.2 $\pm$ 1.3	23.3 $\pm$ 1.3		

^aProbable certified value unless otherwise indicated.^bInformational value only.

were done using x-ray fluorescence. These took place before and after neutron activation. In most cases, the second measurement shows a reduction in the amount of each element. Comparing the first XRFA with NAA results, both Br and Mn displayed about 15% (on the average) higher value by XRFA. A difference in Br values might be ascribed to volatile loss while that for Mn might reasonably relate to other causes (e.g., mechanical loss). The reanalysis by XRFA yielded values

for Mn and Br which generally agreed better with the NAA results. Comparing the first and second XRFA, the values for the soil-related elements Ca and Mn were typically 20% to 30% lower for the second analysis.

This discrepancy can be attributed to handling problems which caused loss of larger particles. This seems to be a reasonable assumption since the specimens are subjected to many shocks both during shipment to Livermore and back to Berkeley

Table 16. NBS-EPA coal - fly ash comparison (coal $\mu\text{g/g}$, unless indicated),

	U. of Md.	NBS ^a	Battelle N. W.	Livermore	Washington State	Oak Ridge
Na	399 $\pm$ 20		420 $\pm$ 30	313 $\pm$ 22		47 ^c
K				0.23 $\pm$ 0.01		0.385 ^c
Ca	0.41% $\pm$ 0.05%			0.42% $\pm$ 0.07%		0.268 ^c
Ba	330 $\pm$ 30			327 $\pm$ 19		317
Cl	970 $\pm$ 110		800 $\pm$ 200	758 $\pm$ 62		652.6
Br	~20			18.6 $\pm$ 2.4		16.0
Al	1.78% $\pm$ 0.16%		1.78% $\pm$ 0.08%	2.0% $\pm$ 0.1%		1.23 ^c
Sc	3.70 $\pm$ 0.25		3.4 $\pm$ 0.3	3.04 $\pm$ 0.19		5.06
Ti	960 $\pm$ 100		1110 $\pm$ 200	1060 $\pm$ 120		789
V	37.0 $\pm$ 3.3	35 $\pm$ 3	33.0 $\pm$ 4	38.3 $\pm$ 3.3	36 $\pm$ 3.8	26.4
Cr	19.7 $\pm$ 1.0	20.2 $\pm$ 0.5	19 $\pm$ 2	19.3 $\pm$ 0.97	21.25 $\pm$ 0.43	
Mn	45.2 $\pm$ 3.2	40 $\pm$ 3	41 $\pm$ 6	47.6 $\pm$ 3.4		38.6
Fe	0.86% $\pm$ 0.06%	0.87% $\pm$ 0.03%	0.81% $\pm$ 0.07%	0.82% $\pm$ 0.04%		
Co	5.6 $\pm$ 0.3	6 ^b	5.2 $\pm$ 0.4	6.4 $\pm$ 0.28		
Zn	~30	37 $\pm$ 4	37 $\pm$ 4			
As	5.7 $\pm$ 0.5	5.9 $\pm$ 0.6		5.04 $\pm$ 0.66	11.23 $\pm$ 0.33	
Sb	4.3 $\pm$ 3.0		3.7 $\pm$ 2.0	4.1 $\pm$ 5.3		4.4
In				0.20 $\pm$ 0.12		
Hf	0.95 $\pm$ 0.08		0.97 $\pm$ 0.1	0.72 $\pm$ 0.06		
W				0.62 $\pm$ 0.27		
La	11.3 $\pm$ 0.6		10.5 $\pm$ 0.5	9.1 $\pm$ 0.38		12.8
Ce	20.4 $\pm$ 1.5			18.5 $\pm$ 0.65		
Sm	1.83 $\pm$ 0.09		1.7 $\pm$ 0.3	1.48 $\pm$ 0.07		
Eu	0.38 $\pm$ 0.03		0.28 $\pm$ 0.01	0.32 $\pm$ 0.01		
Th	3.0 $\pm$ 0.3	3.0 ^b	3.45 $\pm$ 0.18	2.97 $\pm$ 0.17		
U						1.26

^aProbable certified value unless otherwise indicated.^bInformational value only.

and during the irradiation process which involves the use of a pneumatic sample transport system into and out of the reactor.

Table 19 shows comparison of the same four elements on impactors and total and after filters.

Analysis of Aluminum by INAA and Atomic Absorption Analysis (AAS)

During ACHEX-I, an unresolved discrepancy was discovered for the analysis

of Al by INAA and AAS. The aerosol samples were collected on high-volume Whatman 41 air filters. AAS analyses were done at AIHL on 100-130 cm² of the filter and consisted of LiBO₂ fusion, dissolution and aspiration. The average NAA/AAS ratio for the 23 filters is 0.639. The individual values have a correlation factor of 0.85 which suggests a systematic difference between the two procedures.

Table 17. First XRFA intercomparison study - ratio of A and C averages to gravimetric standards.

Set No.	Sample type	Al	K	V	Mn	Fe	Cr	As	Pb
1	A	1.00(0.21)	0.76(0.06)	0.64(0.06)	0.77(0.20)	0.53(0.07)	0.43(0.07)	0.57(0.07)	0.74(0.06)
	C	0.73(0.07)	0.53(0.10)	0.53(0.08)	0.57(0.10)	0.50(0.10)	0.57(0.07)	0.74(0.06)	
2	A	1.73	0.72	0.75	0.67	0.79	0.61	0.69	
	C	0.71	0.71	0.83	0.74	0.75	0.63	0.69	
3	A	0.92(0.07)	0.71(0.07)	0.57(0.07)	0.91(0.03)	0.72(0.04)	0.50(0.04)	0.54(0.03)	
	C	0.51(0.07)	0.60(0.06)	0.92(0.04)	0.79(0.04)	0.71(0.03)	0.57(0.03)	0.53(0.03)	
1.1.1	A	0.75(0.04)	0.71(0.04)	0.94(0.02)	0.84(0.01)	0.89(0.19)			
1.1.1	C	0.75(0.08)	0.87(0.01)	0.96(0.02)	0.83(0.01)	1.20(0.15)			
5	A	0.82(0.02)	1.01(0.02)	0.99(0.03)	0.92(0.02)	1.00(0.03)	0.94(0.03)	1.05(0.03)	
	C	0.81(0.03)	0.95(0.04)	0.95(0.03)	0.91(0.03)	0.99(0.03)	0.94(0.03)	0.99(0.03)	
6	A	1.55(0.20)	0.94(0.01)	0.92(0.01)	1.01(0.02)	1.01(0.01)	0.76(0.07)	0.98(0.05)	
	C	2.11(0.37)	1.01(0.01)	1.04(0.01)	0.95(0.02)	0.96(0.01)	0.88(0.02)	1.20(0.08)	0.92(0.03)
7	A	1.36(0.12)	0.95(0.06)	0.90(0.06)	1.10(0.07)	1.00(0.05)	0.92(0.04)	0.86(0.06)	1.00(0.05)
	C	1.73(0.11)	1.15(0.07)	1.12(0.08)	1.17(0.08)	1.06(0.04)	1.07(0.06)	0.88(0.05)	1.01(0.05)
8	A	1.06(0.16)	1.01(0.15)	1.12(0.17)	1.11(0.17)	0.97(0.16)	1.03(0.15)	0.96(0.15)	
	C	1.03(0.15)	1.57(0.16)	1.02(0.15)	1.09(0.16)	1.11(0.17)	1.15(0.17)	1.06(0.16)	
9	A	0.98	0.90	0.98	1.01	1.00	1.03		
	C	1.04	1.10	1.16	1.17	1.11			
10	A	1.46(0.25)	1.28(0.18)	1.15(0.17)	1.21(0.19)	0.93(0.13)	0.74(0.23)	1.10(0.25)	1.13(0.27)
	C	1.76(0.26)	1.25(0.20)	0.91(0.14)	1.11(0.18)	0.86(0.12)	0.86(0.10)	1.05(0.24)	1.09(0.24)
11	A	0.71	0.92(0.06)	1.10(0.06)	1.03(0.08)	1.01(0.08)	0.98(0.09)	0.93(0.12)	0.84(0.08)
	C	0.58	0.92(0.06)	1.17(0.09)	1.09(0.08)	1.08(0.08)	0.92(0.07)	1.06(0.17)	0.81(0.09)
12	A	6.5 (2.1)	1.13(0.18)	0.99(0.07)	1.01(0.09)	1.01(0.11)	1.01(0.12)	1.08(0.15)	1.04(0.10)
	C	5.0 (1.3)	1.10(0.15)	1.02(0.10)	1.06(0.12)	1.11(0.12)	1.04(0.10)	1.18(0.16)	1.07(0.11)

The analysis of NBS SRM-1632 and NBS SRM-1633 by INAA shows good agreement with other laboratories, although Al is not certified (see Tables 14 and 15). The first XRFA Intercomparison Study results show a reasonable agreement within errors between INAA and XRFA for Al.

The AAS analysis of NBS certified standard have shown good accuracy for Al. The results of INAA and AAS analyses of "standards" do not offer any explanation for the discrepancy between the two pro-

cedures. A possible source of error for INAA would be loss of large particles either during sample transit or during pneumatic insertion and removal of samples from the reactor. During ACHEX-II, sample handling and procedures were revised to largely eliminate the effects of such particle loss.

EPISODIC DATA

Figures 3-6 show Q2 spectra taken of stages 1A, 1B, 4 and the after filter,

Table 18. Comparison of data determined by INAA (L.L.) and XRF (LBL).^a

Specimen		Ca	Ti	Mn	Br
TA0151HV	XRF-1	1470 ± 70	210 ± 42	46 ± 4	302 ± 12
	INAA	1329 ± 450	125 ± 50	34 ± 1	259 ± 9
	XRF-2	1120 ± 60	124 ± 36	34 ± 3	252 ± 10
TB0153HV	XRF-1	2060 ± 100	308 ± 85	76 ± 5	749 ± 30
	INAA	2526 ± 660	326 ± 81	58 ± 2	555 ± 16
	XRF-2	1610 ± 80	226 ± 67	59 ± 4	634 ± 25
TC0153HV	XRF-1	2530 ± 130	328 ± 106	83 ± 6	733 ± 29
	INAA	2278 ± 328	301 ± 93	64 ± 2	639 ± 23
	XRF-2	1930 ± 100	240 ± 73	59 ± 5	642 ± 26
TD0154HV	XRF-1	2110 ± 110	270 ± 77	64 ± 6	568 ± 28
	INAA	1843 ± 754	251 ± 92	46 ± 2	521 ± 15
	XRF-2	1700 ± 70	183 ± 52	42 ± 6	534 ± 21
TE0155HV	XRF-1	1340 ± 70	209 ± 28	48 ± 3	221 ± 9
	INAA	1400 ± 484	290 ± 128	34 ± 1	420 ± 15
	XRF-2	984 ± 49	123 ± 32	33 ± 3	407 ± 16
UF0156HV	XRF-1	1890 ± 90	275 ± 61	71 ± 4	473 ± 19
	INAA	2249 ± 247	297 ± 67	59 ± 2	433 ± 16
	XRF-2	1560 ± 80	193 ± 53	58 ± 4	432 ± 17
VH0158HV	XRF-1	3780 ± 190	289 ± 43	92 ± 4	289 ± 12
	INAA	4764 ± 369	219 ± 63	80 ± 3	217 ± 6
	XRF-2	3240 ± 160	192 ± 44	80 ± 4	257 ± 10
VI0159HV	XRF-1	3730 ± 190	300 ± 42	89 ± 4	312 ± 12
	INAA	4705 ± 376	355 ± 65	74 ± 2	260 ± 9
	XRF-2	2980 ± 150	194 ± 50	72 ± 4	269 ± 11
VJ0160HV	XRF-1	3150 ± 160	384 ± 46	86 ± 5	162 ± 6
	INAA	2706 ± 321	265 ± 64		131 ± 4
	XRF-2	1810 ± 90	185 ± 28	42 ± 4	130 ± 5
WK0161HV	XRF-1	1280 ± 60	152 ± 85	42 ± 3	251 ± 10
	INAA	1308 ± 77	181 ± 56	40 ± 1	203 ± 6
	XRF-2	1120 ± 60	114 ± 81	37 ± 3	223 ± 9
WL0163HV	XRF-1	1450 ± 70	199 ± 44	54 ± 4	1190 ± 50
	INAA	1936 ± 60	< 148	44 ± 2	1212 ± 34
	XRF-2	1100 ± 60	125 ± 51	40 ± 3	1140 ± 50

^aR. Glaucque, 5/2/74.

Table 19. Comparison of data determined by INAA (LLL) and XRF (LBL).^a

Specimen		Ca	Ti	Mn	Br
TB0260SAL	XRF-1	395 ± 60	73 ± 7	5 ± 2	16 ± 1
	INAA	743 ± 189	158 ± 43	23.7 ± 1	16.8 ± 0.5
TB0261SBL	XRF-1	≤ 60	6 ± 5	≤ 6	11 ± 1
	INAA	119 ± 70	35 ± 9	4.4 ± 0.43	12.2 ± 0.36
TB0262S2L	XRF-1	204 ± 57	17 ± 6	3 ± 2	21 ± 1
	INAA	177 ± 81	46 ± 126	8.7 ± 0.59	22.4 ± 0.65
TB0263S3L	XRF-1	325 ± 59	29 ± 6	4 ± 2	53 ± 2
	INAA	313 ± 87	51 ± 11	7.1 ± 0.6	43 ± 1.2
TB0264S4L	XRF-1	≤ 60	≤ 15	≤ 7	107 ± 4
	INAA	15.5 ± 56	16.1 ± 8.7	4.4 ± 0.4	90 ± 2.5
TB0766AFL	XRF-1	166 ± 30	≤ 40	9 ± 5	488 ± 20
	INAA	225.6 ± 264.5	≤ 52.2	15.3 ± 1.3	417.4 ± 11.3
TB0516TF	XRF-1	2090 ± 80	392 ± 98	93 ± 7	735 ± 29
	INAA	1700 ± 800	455 ± 244	53 ± 2.4	670 ± 19
UC0300SAL	XRF-1	589 ± 30	149 ± 24	18 ± 3	16 ± 2
	INAA	405 ± 372	138 ± 39	13.7 ± 0.8	13.6 ± 0.4
UF0301SBL	XRF-1	93 ± 15	28 ± 5	5 ± 2	8 ± 2
	INAA	≤ 7.6	23 ± 7	2.5 ± 0.35	8.1 ± 0.25
UF0302S2L	XRF-1	172 ± 17	26 ± 5	7 ± 3	20 ± 2
	INAA	267 ± 171	42 ± 10	5.2 ± 0.4	19.1 ± 0.6
UF0303S3L	XRF-1	214 ± 17	40 ± 17	10 ± 3	51 ± 2
	INAA	367 ± 87	22.1 ± 10	10.2 ± 0.63	45 ± 1.3
UF0304S4L	XRF-1	58 ± 15	≤ 18	5 ± 3	140 ± 6
	INAA	45 ± 117	≤ 23.6	6.6 ± 0.5	114 ± 3
UF0813AFL	XRF-1	35 ± 29	≤ 35	20 ± 5	272 ± 11
	INAA	99.3 ± 139	≤ 44	12.6 ± 1.2	231 ± 6.6
UF0670TF	XRF-1	2110 ± 80	395 ± 94	84 ± 7	507 ± 20
	INAA	1890 ± 1636	392 ± 98	58 ± 2.5	456 ± 13
VH0340SAL	XRF-1	584 ± 29	73 ± 6	14 ± 3	8 ± 2
	INAA	1098 ± 179	136 ± 33	21 ± 1	6.3 ± 0.2
VH0341SBL	XRF-1	241 ± 17	30 ± 12	5 ± 2	4 ± 1
	INAA	373 ± 88	36 ± 9	10.7 ± 0.6	3.5 ± 0.13
VH0342S2L	XRF-1	400 ± 20	44 ± 17	7 ± 2	12 ± 2
	INAA	473 ± 99	55 ± 12	8.6 ± 0.6	9.5 ± 0.3
VH0343S3L	XRF-1	453 ± 23	44 ± 6	8 ± 3	24 ± 2
	INAA	538 ± 271	48.6 ± 12	8.1 ± 0.6	21 ± 0.6
VHC344S4L	XRF-1	63 ± 15	≤ 15	≤ 7	59 ± 2
	INAA	275 ± 156	≤ 17.6	2.7 ± 0.38	59 ± 1.7

Table 19 (continued)

Specimen		Ca	Ti	Mn	Br
VH0853AFL	XRF-1	107 ± 29	≤24	≤12	145 ± 6
	INAA	218 ± 256	≤31	6.6 ± 1.1	144 ± 4
VH0792TF	XRF-1	3280 ± 130	340 ± 39	69 ± 6	294 ± 12
	INAA	4381 ± 526	375 ± 82	55 ± 2.4	266 ± 7.5
V10330SAL	XRF-1	1410 ± 70	148 ± 17	28 ± 3	5 ± 1
	INAA	2537 ± 68	232 ± 67.6	33.4 ± 1.32	5.36 ± 0.180
V10331SBL	XRF-1	687 ± 34	68 ± 17	9 ± 3	5 ± 2
	INAA	759.6 ± 137	98 ± 24	12 ± 0.656	5.26 ± 0.161
V10332S2L	XRF-11	584 ± 29	69 ± 20	13 ± 2	7 ± 1
	INAA	676 ± 117.6	84.4 ± 18.4	11.5 ± 0.642	7.14 ± 0.214
V10333S3L	XRF-1	474 ± 20	48 ± 6	8 ± 2	19 ± 2
	INAA	565 ± 114.5	42.1 ± 10.4	8.16 ± 0.640	21.98 ± 0.637
V10334S4L	XRF-1	76 ± 16	≤21	6 ± 3	107 ± 4
	INAA	270.8 ± 89	≤22.81	3.57 ± 0.464	101.8 ± 2.89
V101125AFL	XRF-1	193 ± 29	≤30	≤14	129 ± 5
	INAA	156.1 ± 140	≤31.6	5.34 ± 1.06	116.1 ± 3.3
V10806TF	XRF-1	8830 ± 440	815 ± 129	141 ± 8	294 ± 5
	INAA	7506 ± 2764	918.2 ± 202	118.7 ± 4.1	258 ± 7.3
TD0280SAL	XRF-1	619 ± 71	91 ± 7	17 ± 3	15 ± 1
	INAA	663 ± 155	112 ± 29	14.5 ± 0.8	8.5 ± 0.26
TD0281SBL	XRF-1	≤80	≤15	≤7	8 ± 1
	INAA	147 ± 76	18 ± 7	3.9 ± 0.4	7.5 ± 0.23
TD0282S2L	XRF-1	179 ± 57	18 ± 6	6 ± 2	20 ± 1
	INAA	417 ± 95	59 ± 12	7.9 ± 0.6	15.5 ± 0.46
TD0283S3L	XRF-1	206 ± 58	18 ± 6	≤8	38 ± 2
	INAA	299 ± 86	42 ± 11	6.5 ± 0.6	37 ± 1
TD0284S4L	XRF-1	≤60	≤15	≤8	98 ± 4
	INAA	43 ± 63	18 ± 9	4.1 ± 0.43	88 ± 2.5
TD0786AFL	XRF-1	111 ± 27	18 ± 10	≤13	202 ± 8
	INAA	131 ± 137	< 37.2	3.8 ± 1.0	183 ± 5.2
TD0643TF	XRF-1	1310 ± 50	233 ± 53	42 ± 6	393 ± 16
	INAA	1022 ± 591	154 ± 41	25.2 ± 1.8	350 ± 9.9
WL0350SAL	XRF-1	102 ± 15	15 ± 11	3 ± 2	9 ± 1
	INAA	193.6 ± 380	27.6 ± 8.7	4.58 ± 0.926	9.57 ± 0.292
WL0351SBL	SRF-1	35 ± 15	14 ± 5	≤7	8 ± 1
	INAA	118 ± 114	5.54 ± 4.80	1.12 ± 0.75	6.09 ± 0.199
WL0352S2L	XRF-1	101 ± 16	14 ± 10	≤7	12 ± 2
	INAA	65.7 ± 66.9	≤14.9	1.9 ± 0.37	11.9 ± 0.355

Table 19 (continued)

Specimen		Ca	Ti	Mn	Br
WL0353S3L	XRF-1	114 ± 16	21 ± 5	<7	30 ± 2
	INAA	91.6 ± 7.6	14.1 ± 6.77	2.24 ± 0.388	25.2 ± 0.729
WL0354S4L	XRF-1	41 ± 15	<15	4 ± 2	39 ± 2
	INAA	35.3 ± 63.1	<16	3.07 ± 0.384	40.0 ± 1.15
WL1038AFL	XRF-1	84 ± 29	<31	13 ± 5	160 ± 6
	INAA	158 ± 234	<35	6.0 ± 1.1	123.5 ± 3.5
WL1096TF	XRF-1	424 ± 37	<89	26 ± 6	220 ± 9
	INAA	569 ± 273	81.1 ± 29.8	14.6 ± 1.4	178 ± 5.1
WK0320SAL	XRF-1	188 ± 16	35 ± 11	6 ± 2	7 ± 1
	INAA	201.7 ± 89.6	80.4 ± 17.2	<0.0081	5.48 ± 0.181
WK0321SBL	XRF-1	28 ± 15	15 ± 5	<6	5 ± 1
	INAA	7.17 ± 62.0	16.5 ± 5.26	1.85 ± 0.299	3.24 ± 0.126
WK0322S2L	XRF-1	110 ± 16	<15	<7	11 ± 2
	INAA	55.9	17.0 ± 6.81	3.78 ± 0.436	8.63 ± 0.265
WK0323S3L	XRF-1	174 ± 16	20 ± 8	7 ± 2	26 ± 2
	INAA	222 ± 155	22.0 ± 9.24	4.60 ± 0.534	23.1 ± 0.667
WK0324S4L	XRF-1	65 ± 16	27 ± 8	<8	61 ± 2
	INAA	12.8 ± 54.1	15.5 ± 9.698	6.86 ± 0.508	50.6 ± 1.43
WK1109AFL	XRF-1	97 ± 30	27 ± 11	<14	89 ± 4
	INAA	101 ± 131	<29	2.36 ± 0.95	70 ± 2
WK1084TF	XRF-1	693 ± 37	123 ± 30	33 ± 6	214 ± 9
	INAA	1184 ± 494	126 ± 49	26.7 ± 1.7	154 ± 4.4

^aR. Glaucque, 1/25/74.

respectively, of a 24-hour Lundgren impactor run at Dominguez Hills, California on October 5, 1973 in ACHEX-II. The aerodynamic diameters were 8-15 μ for stage 1, 4-8 μ for stage 2, 1.5-4 μ for stage 3, 0.5-1.5 μ for stage 4, and <0.5 μ for stage 5. The Lundgren impactors used in ACHEX had two stage 1's - that is, stages 1A and 1B had the same size slits. The Lundgrens were modified this way in order to completely collect all particles in the 8-15 μ range where bounce-off problems are severe. By comparing Figures 3-6, one can see the decrease of

Al, Ca, Na, and the increase of Cl, V, and Br with decreasing particle size. Figure 7 shows a 2-hr total filter spectrum taken from 10-1200 at Dominguez Hills while the 24-hr impactor run was taking place. Analyses of these types of spectra yield elemental diurnal variations over 24-hr with 2-hr intervals.

Figures 8-12 illustrate the kind of data produced by INAA and how they are used in the experimental interpretations. The analyses can be divided into two types: diurnal patterns, and particulate size distributions. Figures 8 and 9 shows the

Fig. 3. Gamma-ray spectrum of Dominguez Hills impactor sample collected on 10/5/73 from 2100 to 2100, stage 1A. Numbers in parentheses indicate (nanograms/nanograms per cubic meter).

Fig. 4. Gamma-ray spectrum of Dominguez Hills impactor sample collected on 10/5/73 from 2100 to 2100, stage 1B. Numbers in parentheses indicate (nanograms/nanograms per cubic meter).

Fig. 5. Gamma-ray spectrum of Dominguez Hills impactor sample collected on 10/5/73 from 2100 to 2100, stage 4. Numbers in parentheses indicate (nanograms/nanograms per cubic meter).

Fig. 6. Gamma-ray spectrum of Dominguez Hills impactor sample collected on 10/5/73 from 1000 to 1200 after filter. Numbers in parentheses indicate (nanograms/nanograms per cubic meter).

Fig. 7. Gamma-ray spectrum of Dominguez Hills impactor sample collected on 10/5/73 from 1000 to 1200 total filter. Numbers indicate total nanograms detected.

Harbor Freeway episode of September 20, 1972. Lundgren impactor substrates were cut into two-hour segments and the Gelman GA-1 after filters were changed every 2 hr. Samples were collected one block from the freeway. Figure 8 shows the particle size distributions for Br, Na, Cl, and Al for early morning and late afternoon commuter periods. Figure 9 shows the diurnal patterns of Pb, Br, Na, Cl, Al, V, and total mass for the after filters ($< 0.5 \mu$ particles) for the 24-hr period. The Pb data are taken from Bob Glaque at Lawrence Berkeley Laboratory.¹⁰

Fig. 8. Particle size distribution of Br, Cl, Na, Al, collected at Harbor Freeway, 9/20/73.

In Figure 9 the Cl, Br, and Pb diurnal patterns track each other throughout the day, indicating a common submicron particle source, namely lead halide emissions from auto exhausts. On the other hand Al, V, and Na each portray different diurnal patterns and different sources.

The Br distribution in Figure 8 is peaked on submicron particles, typical of an auto-engine combustion source, with 92% (morning) and 82% (evening) on the after filters. The Pb Br ratios for the after filters are 2.1 (morning) and 2.0 (evening) which are typical of fresh exhaust, while the Pb Br ratio in ethyl gasoline is 2.5.

Although the Cl diurnal pattern is the same as for Br, the Cl is less concentrated on submicron particles as is Br, the per-

centages being 78% (morning) and 35% (evening). The Cl distribution resembles the Na distribution in the micron range. It appears that most of the submicron Cl is from auto exhaust while most of the supermicron Cl is from the marine aerosol. Stages 1-4 show a deficiency of Cl relative to a sea water Na/Cl ratio of 0.55 at 0500-0700 [0.98(1), 1.4(2), 2.5(3), and 2.7(4)]. At 1700 to 1900, the Na/Cl ratio is closer to 0.55 [0.72(1), 0.64(2), 0.65(3), and 1.2(4)]. On the after filters the Na/Cl ratios are 0.04 (morning) and 0.1 (evening). These data are consistent with a Cl loss during the morning hours, probably due to oxidizing agents which release Cl to Cl_2 gas.

Aluminum shows a predominance of large particles in Figure 8, typical of soil-derived aerosols, with only 1.6% (morning) and 2.2% (evening) on the after filter. Sodium is distributed more uniformly in the 1-10 μ range. The peaking of the Na distribution on stage 3 (1.5-4.0 μ) is considered to be representative of the marine aerosol. Although we do not show distributions for V, they show V peaked on submicron particles, indicating a combustion source.

Figure 10 shows the diurnal patterns of Na, Br, Cl, Al, V, and mass on Gelman GA-1 total filters taken in the August 24, 1972 Pasadena episode. Note that V correlates with total mass, both peaking at 1300 to 1700. The Na concentration remains constant, indicating a constant background. In this episode the total Cl does not follow the total Br or Na. It is not known why Cl and Al both show a minimum at 1500 to 1700.

At Fresno Fairgrounds on September 1, 1972, total Br and Pb correlate showing a

Fig. 9. Diurnal patterns of selected elements at Harbor Freeway, 9/20/73.

Fig. 10. Diurnal patterns of selected elements at Pasadena, 8/24/72.

peak at 0600. However, Al, Mn, and V, show similar patterns, but unlike Pb and Br. At Fresno, the particle size distributions (not shown) show Na, V, and Al have substantial large particle (8-15 μ) components, indicating a soil source. Because of Fresno's inland location, we would expect negligible marine Na. The Cl minimum at 1500 to 1700 is not understood.

Figure 12 show after-filter diurnal patterns at Pomona on October 24-25, 1972 for submicron Br, Pb, Cl, Na, and Al. Again, as at the previous sites discussed, Br and Pb correlate, while Al shows a unique diurnal pattern. Submicron Cl does not appear to correlate with Pb and Br; however, it appears to more closely follow the pattern of Na.

Fig. 11. Diurnal patterns of selected elements at Fresno, 9/1/72.

Fig. 12. Diurnal patterns of selected elements at Pomona, 10/24/72.

Summary

The State of California Air Resources Board sponsored a major experiment in the chemistry of aerosols in urban and non-urban sites of California from 1972 to 1974. The main objectives of this Aerosol Characterization Experiment (ACHEX) were:

1. To characterize aerosols in terms of their physical and chemical properties.
2. To investigate the origins and evolution of aerosols.
3. To estimate the primary and secondary aerosol contributions to the total airborne particulate concentration in the Los Angeles Basin.
4. To evaluate the significance of anthropogenic sources.

Elemental analysis of intensive and episodic collections of aerosols, together with meteorological data, was the method used to estimate natural and anthropogenic sources of airborne particulates. Elemental data, combined with other chemical and physical data, also aided the study of secondary aerosol formation. Instrumental neutron activation analysis (INAA) was one of the techniques used to measure elemental diurnal variations and to determine elemental particle size distributions.

The ACHEX data on the distribution of aerosol composition with size confirm the hypothesis that constituents originating from certain classes of sources dominate the mass in particular size ranges. Primary material from combustion, chemical, and metal refining sources, such as Br, Cl, and V, appear strongly in the submicron (or anthropogenic) fraction. The natural or quasinatural elements such as Na, Cl, Al, Fe, Ca, and Sc appear in the supermicron fractions. In this study the natural background aerosol consisted of a mixture of sea salt, soil dust, and a residue of aged aerosol transported from distances away from an urban area.

A secondary role of INAA was the validation of other analytical techniques utilized in the chemical analysis of aerosols. Supplemental experiments were also performed using INAA to validate the collection efficiencies of rotating-state cascade impactors.

As a result of these studies, it was concluded that techniques using INAA were useful operational methods for chemical analysis of aerosol samples taken over two-hour periods in urban air in an active monitoring program.

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