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TRACE ELEMENT ANALYSIS AT THE LIVERMORE POOL-TYPE REACTOR USING NEUTRON ACTIVATION TECHNIQUES

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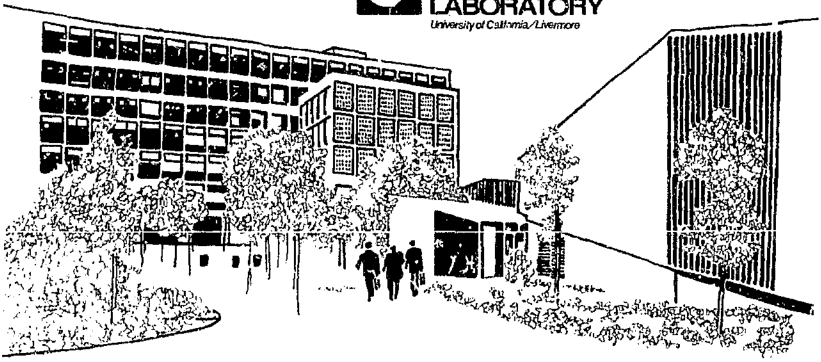

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Abstract

Instrumental Neutron Activation Analysis is a technique of trace analysis using measurements of radioactivity induced in the sample by exposure to a source of neutrons. The induced activity is measured by detecting the emitted gamma radiation. Each Gamma emitter can then be identified by the energy of the photopeaks produced as the nuclide decays toward its ground state, and by the half-life of the neutron-induced activity. A complex computer program, GAMANAL, has been used which can accomplish the major tasks of nuclide identification and quantification. A description of the methods employed at the Livermore Pool-Type Reactor (LPTR) is discussed, including sample preparation, irradiation, analysis, and application of the technique.

Introduction

The purpose of this report is to describe the capabilities of Trace Element Analysis at the Livermore Pool Type Reactor (LPTR) using Instrumental Neutron Activation Analysis (INAA). The technology and the methods employed will be discussed, including sample preparation, irradiation, and analysis. Applications of the INAA technique in past and current projects will be described.

SCOPE OF TRACE ELEMENT ANALYSIS

Trace element analysis at the LPTR has been primarily concerned with research programs. The involvement takes place at various levels of interaction; from definition of problems through finished reports. In addition, a service is provided within the Laboratory for trace element analysis. The users of the service are given as much assistance as desired. Applied research and development contracts are also carried out with groups outside the Laboratory.

Some areas that have been investigated are:

1. Trace elements in aerosols
   a. Air sampling in the vicinity of smelting operations in Kellogg, Idaho[1]
   b. ACHEX (California Aerosol Characterization Experiment)[2]
2. Trace elements in milk
3. Trace elements in environmental samples
   a. Soils/sediments/sludge[3]
   b. Vegetation
   c. Water — fresh/marine
4. Trace elements in marine organisms
5. Forensic analysis
   a. Jewelry tagging for identification
   b. Diamond tagging
   c. Gunshot residue analysis

Some of these projects are described in the section on applications.

Description of the Technique

The INAA method of trace element identification has become increasingly more important with the progressive improvement in sensitivity. This improved sensitivity has been made possible by the use of high-resolution, solid-state radiation detectors, improved data-collection and data-reduction techniques, and increased experience in sample preparation and collection methods.

One of the chief advantages of INAA is that it is usually a non-destructive analytical technique which requires little or no chemical pre-treatment. It also provides the ability to look at isotopic concentrations as well as elemental concentrations for some isotopes. The word "Instrumental" in this context means that element or isotope identification is accomplished by instruments without resorting to chemical separation.

Most INAA is done using thermal neutrons from a nuclear reactor. Neutron fluxes of 10^{12} to 10^{14} n/cm^2/sec (neutrons per square centimeter per second) can be easily obtained at most reactor facilities, with fluxes of 10^{16} n/cm^2 obtainable at some of the pulsed research reactor facilities. However, pulsed reactor fluxes are useful only when looking at elements with induced activities having half-lives on the order of tenths-of-seconds. Recently some INAA has been performed using ^{252}Cf sources with fast neutrons having energies up to 14 MeV.

BASIC PRINCIPLES

Instrumental neutron activation analysis is based on the measurement of radioactivity induced in the sample after exposure to a source of neutrons. This induced activity is most easily determined by detecting the emitted gamma radiation with a gamma spectrometer which characterizes the gamma emissions present. This characterization gives the energy and absolute intensity of each gamma ray. Figure 1 is a schematic representation of the method.

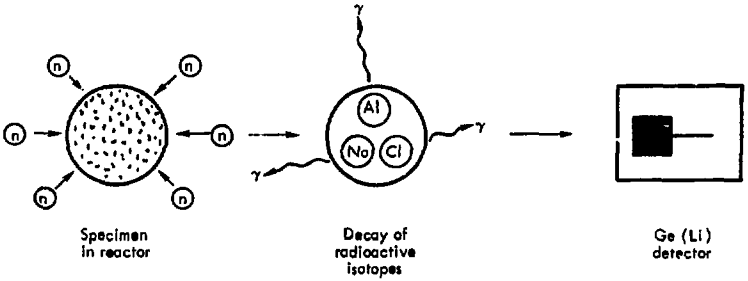

Fig. 1 Schematic diagram of Instrumental Neutron Activation Analysis Procedure.

Once the gamma spectrum is obtained, it is necessary to identify the mixture of nuclides which will account for the complex spectrum. Each gamma emitter can be identified by the energy (or energies) of the photopeaks produced as the nuclide decays towards its ground state, and by the half-life of the neutron-induced activity. Most elements which have a useful cross-section for neutron capture, produce at least one isotope which can be used for a unique identification based on half-life and gamma peaks. A complex computer program has been developed which can accomplish the major tasks of nuclide identification and quantitation. This program, GAMANAL, will be discussed later.

The identification of the nuclide present in an activated sample does not immediately yield an elemental analysis in a useful form. It is necessary to translate absolute information, such as disintegrations per minute or atoms present at zero time, into parts per million, or total ng, etc. This can be accomplished in two ways. The first would involve calculations based on measured neutron flux, cross-sections, and exposure times. This is fundamentally possible, but is totally dependent on precise knowledge of a number of measured parameters. Thus, the cumulative uncertainties of a large number of measurements makes the final answer quite unreliable. The second method is to simultaneously irradiate a mixture of known amounts of the elements in question and to determine the unknown by direct ratio of activities. This method has the advantage of being independent of any absolute measurements, and in addition, gives an analysis of the natural element rather than individual isotopes as in the first method. A second computer program has been developed to take the data produced by GAMANAL and produce the final analysis based on the second method.

In most, if not all samples, there are competing activities to be considered. The samples usually contain many trace elements as well as the principle ones. The activation and counting scheme employed must be chosen in such a manner as to optimize the activity of as many elements as reasonably possible. This usually involves making two or more separate irradiations for each sample, and applying various counting schedules depending on the type of sample and the elements being sought in the analysis. This is an effective method of utilizing the half-lives to separate elements into groups, thus reducing the complexity of the spectral mix and producing less ambiguous identifications. In addition, a strong interference produced by a major component such as sodium can be allowed to die away leaving the longer lived trace elements still amenable to analysis.

IRRADIATION AND COUNTING PROCEDURE

A typical irradiation schedule and counting scheme is 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.

The irradiation and counting scheme (Table 1) was designed to give the maximum sensitivity for a wide range of elements. The scheme is similar to that used by others for the same type of analyses.

Table 1. Neutron-irradiation and sample-counting schedule.

Irradiation time	Neutron flux ($n/cm^2/sec$)	Cooling time	Counting time	Elements detected
2 min	2×10^{13}	4 min	500 sec	Al, V, Cu, Ti, Ca
		20 min	1000 sec	Na, Mg, Cl, Mn, Br, I, Ba, In
12 hr	4×10^{12}	20-30 hr	2000 sec	As, W, Ga, K, Cd
		6-10 days	100 min	Sm, Au, Hg, La, Sb
		20-30 days	8-12 hr	Fe, Cr, Co, Zn, Hg, Se, Ag, Sb, Ce, Eu, Sc, Th, Ni, Ta, Hf, Ba, Rb

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

Table 2 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. It shows that ^{65}Zn 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 using detectors with resolutions that are currently available. 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 the GAMANAL program, it is possible to resolve large amounts of ^{110m}Ag, ^{46}Sc, and ^{65}Zn in the same sample. A close examination of Table 2 reveals several other interferences of the type discussed above which occur in a typical sample.

The Neutron Source

The neutron source used to activate samples is the Livermore Pool Type Reactor (LPTR) which is a light-water moderated and cooled reactor consisting of plate-type fuel elements and boron-containing control rods located in a 7.9 m (26 ft) deep by 1.98 m (6.5 ft) diameter tank. Various beam tubes and irradiation facilities allow access to neutron fluxes ranging as high as 7×10^{13} $n/cm^2/sec$, and gamma dose rates above 10^{10} rad/hr. The reactor is used for basic and applied research in support of Laboratory programs. The reactor is operated on a scheduled basis that permits a routine maintenance period, standard safety system checks, and a maximum operating schedule for experiments and irradiations. The LPTR's User's Guide[4] describes the experimental irradiation facilities and services that are available.

The Detector System

The ability to analyze the samples, once they have been irradiated, is of primary importance.

Table 2. Parent, daughter, half-life, and energy of observed gamma rays for elements analyzed by INAA at the LPTR.

Parent element exposed	Daughter isotope observed	Half-life[a]	Gamma-ray energy observed[b] (keV)
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	492.3(29.5), 527.9(100)
Sm	$^{153}_{62}Sm$	46.8 h	103.2(100)
Au	$^{198}_{79}Au$	64.7 h	411.8(100)

Table 2. (Continued)

Parent element exposed	Daughter isotope observed	Half-life[a]	Gamma-ray energy observed[b] (keV)
La	$^{140}_{57}\mathrm{La}$	40.2 h	328.8(21.4), 487.0(49.4), 1596.6(100)
Fe	$^{59}_{26}\mathrm{Fe}$	45.6 d	1099.3(100), 1291.5(77.0)
Cr	$^{51}_{24}\mathrm{Cr}$	27.8 d	320.1(100)
Co	$^{60}_{27}\mathrm{Co}$	5.26 y	1173.2(100), 1332.5(100)
Zn	$^{65}_{30}\mathrm{Zn}$	24.3 d	1115.5(100)
Hg	$^{203}_{80}\mathrm{Hg}$	46.9 d	279.2(100)
Sc	$^{75}_{34}\mathrm{Sc}$	120. d	136.0(96.0), 264.7(100)
Ag	$^{108m}_{47}\mathrm{Ag}$	5.00 y	434.0(100), 614.4(100), 723.0(100)
Ag	$^{110m}_{47}\mathrm{Ag}$	255. d	657.7(100), 884.7(79.6), 937.5(36.5), 1384.2(27.7)
Sb	$^{124}_{51}\mathrm{Sb}$	60.3 d	602.7(100), 1691.1(5[illegible].2)
Ce	$^{141}_{58}\mathrm{Ce}$	32.5 d	145.5(100)
Eu	$^{152}_{63}\mathrm{Eu}$	12.7 y	121.8(100), 344.2(85.6), 1408.1(65.0)
Sc	$^{46}_{21}\mathrm{Sc}$	83.9 d	889.3(100), 1120.5(100)
Th	$^{233}_{91}\mathrm{Pa}$	27.0 d	311.9(100)
Ni	$^{58}_{27}\mathrm{Co}$	71.3 d	811.1(100)
Hf	$^{175}_{72}\mathrm{Hf}$	70.0 d	343.4(100)
Hf	$^{181}_{72}\mathrm{Hf}$	42.3 d	133.1(49.4), 482.2(100)

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[a] Time units are as follows: m = minutes, h = hours, d = days, y = years.

[b] Numbers given in parenthesis following the gamma ray energy are the relative intensities (%) of the gamma rays.

Figure 2 is a block diagram of the detector system for counting short irradiation samples. It is built around a 40-cm^2 lithium-drifted germanium Ge (Li) detector coupled to a 4096 channel pulse height analyzer and the appropriate linear electronics.

For counting samples subjected to long irradiation, a variety of detectors are available. These are described in Ref. 5. A brief summary is given below.

The gamma counting is accomplished with a variety of Ge(Li)-diode detector systems which are listed in Table 3. The diodes vary in volume from 19 to 50 cc. Three of the counting systems are automated. The automated systems, interfaced to a PDP-8 computer, are capable of handling 16 samples per system, thus allowing 24-hr/day counter use. The remainder of the systems can analyze one sample at a time, and the data are transferred to the PDP-8 system by a manual dump. All data are subsequently transferred to magnetic tape and analyzed on a CDC-7600 computer (described later).

Figure 3 shows a typical sample changer associated with a Ge(Li) detector system. The cryostat and detector are seen to the left of upper center while the lower half of the picture shows the sample holders in the changer. The center of the photograph shows the mechanism for raising a sample into counting position. The whole system is automated under control of the PDP-8 system.

The data derived using the counting scheme shown in Table 1 are recorded on computer-compatible magnetic tape for permanent reference and for subsequent reduction and analysis. The procedure is effective for the identification of 35 elements in a single sample. Other elements are added to the list as the need arises.

Detection Limits

The detection limits for 75 elements are given in Table 4, based on a maximum irradiation time of 1 hr, a thermal neutron flux of 10^{13} n/cm^2/sec, and no appreciable interferences.[1] These detection limits can therefore be thought of as theoretical limits within the state-of-the-art. An example of empirically derived detection limits are shown in Table 5.

Standardization

The standardization methods differ for short and long irradiations. The main similarity in the two methods is that both use premixed solutions containing only those elements of interest. Both have the same shortcoming, namely, that one must prepare standards of approximately the same concentrations as the samples of interest. This necessitates an estimation of the composition of the sample. However, this estimation is critical only if one is looking at samples which contain large amounts of elements that have interfering gamma rays.

For short irradiations all samples are normalized to a "standard flux monitor". Several different types of flux monitors are used by different investigators depending on their specific application, but each is designed to do the same thing, namely, to normalize a given irradiation back to some known condition or parameter.

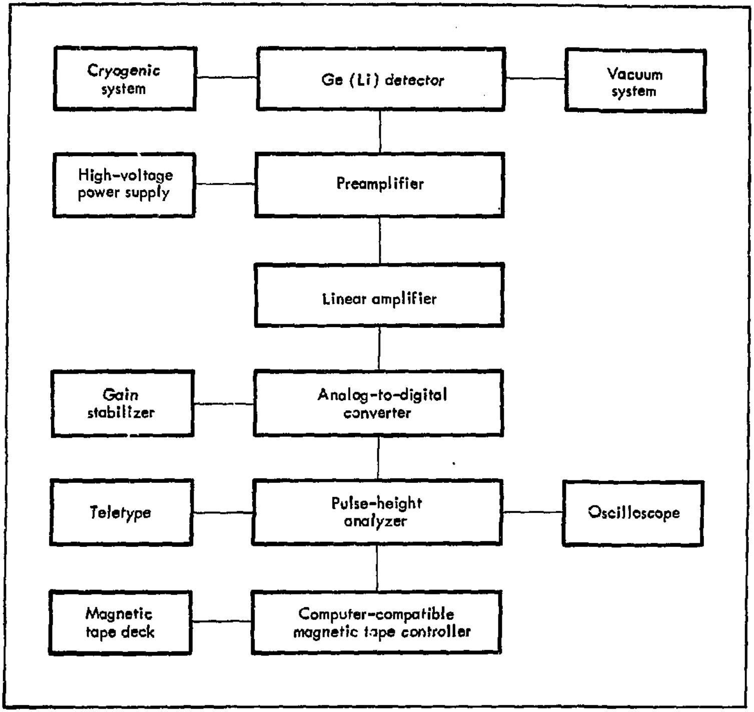

Fig. 2   Block diagram of INAA detector system used for short irradiation counting.

Table 3. Summary of Ge(Li) detectors and systems used for gamma-counting INAA samples.

Detector and system identification	Description
C2	Canberra 45-cc "down-looker," automatic counting chamber No. 2. PDP-8 control and dump.
N1	Nuclear Diodes 40-cc "down-looker," automatic counting chamber No. 1, PDP-8 control and dump.
T3	Princeton Gamma Tech 50-cc "down-looker," automatic counting chamber No. 3, PDP-8 control and dump.
S4	Nuclear Diodes 48-cc "up-looker," manual change, PDP-8 control and dump.
M5	LLL 19-cc "down-looker," manual change, paper tape output.
U8	Nuclear Diodes 25-cc "up-looker," manual change, paper tape output.
W7	Nuclear Diodes 48-cc "side-looker," manual change, paper tape output.
V7	Nuclear Diodes 48-cc "side-looker," manual change, paper tape output.
	All systems except U use 4096-channel analyzers. System U uses a 2048-channel analyzer.

A titanium flux monitor is normally used, and is counted for 60 sec between the 500- and 1000-sec sample counts as shown in Table 1. Several titanium flux monitors are in use. All were irradiated for a predetermined time, counted, and found to be statistically identical so they are used interchangeably. The flux monitors are placed in the same position, with respect to the sample, in the sample carrier during each irradiation. The counts from the sample flux monitor are then proportioned to the master standard flux monitor count, and all elemental counts are then proportioned up or down by the same factor. The proportioning is performed by the data reduction program, and the program "flags" any monitor that deviates from the master monitor by more than 10%, thus signaling the possibility of an error in the irradiation procedure either in positioning, timing, or a shift in flux distribution within the reactor.

To calibrate the detector, we put a standard solution of known elemental composition on a filter paper, irradiate

Fig. 3 Automatic sample changing system utilizing a Ge(Li) detector.

and count the sample along with a Ti flux monitor, and determine the gamma-ray peak area versus the mass for the standard sample. Enough samples are then made up and run to produce a peak area vs sample position for each element of interest. This matrix includes both the standard value as well as the analytical error estimate for each element in the matrix.

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

DATA REDUCTION

The data reduction gamma-ray analysis programs used are MIKEGAM and GAMANAL. MIKEGAM is an adapted version of a technique developed by Ralston and Wilcox.[6] It is written so as to be run under the Monitor System on Lawrence Livermore Laboratory's CDC 6600 computers, and is used primarily for analysis of short irradiation data. GAMANAL is used for the long irradiation data reduction. The accuracy of the codes has been verified by use of interlaboratory and intralaboratory compsriaon studies.

Description of GAMANAL

The GAMANAL code is a general purpose computer program used for data reduction

Table 4. Detection limits of the INAA technique to 75 elements, assuming a 1-hr irradiation with a thermal neutron flux of 10^{13} n/cm^2 sec and no appreciable interferences.

Limit of detection (μg)	
$1-3 \times 10^{-7}$	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

and interpretation of gamma spectra. It examines the pulse-height data for "background" and "peak" regions, fits these peaks with the proper shape functions, and corrects for the effects of geometry, attenuation, and detector efficiency in evaluating the photon emission rate. The program then searches a "library" of decay-scheme information and makes tentative assignments for each of the observed peaks. A matrix of equations is formed so that the intensity of each peak is descibed as a linear addition of the identified nuclides present. The quantitative value, as well as the degree of interference, is the result of a least-squares solution of this set of equations. Unlikely components are also weeded out in this process. A more complete description is given by Gunnink and Niday.[7]

For the neutron activation analysis program, a special library of nuclides is loaded into GAMANAL.

Table 5. Limits of detection[a] for trace elements in aerosols with instrumental neutron activation — ng/m^3.

Element	Gelman GA-1	Impactor film[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		0.02
Ba	2	0.5

[a] Above blank

[b] Average results for 0.0006 cm mylar, 0.0025 cm teflon, and 0.0025 cm polyethylene covered with 0.004 cm sticky resin.

A package of specialized interactive programs is used to convert the raw gamma analysis data from GAMANAL to elemental characterizations.

Typical Output from Instrumental Neutron Activation Analysis Sample

A typical high volume air filter aerosol sample (IAS 21A) is shown as an example of gamma spectra obtained after activation. Figures 4 - 8 are plots of the data for sample 21A resulting from the typical irradiation and counting periods described in Table 1. The irradiation data is shown for each spectrum presented, and insofar as practicable, all peaks have been identified. Some of the peaks have not been identified and labeled because their origin is not known. These unlabeled peaks may be peaks that can be attributed to more than one element, they may be single and double escape peaks, or they may be coincidence sum peaks.

SAMPLE PREPARATION AND HANDLING

General

Sample preparation and handling are of great importance in trace element work. Clean techniques must be observed at every step prior to irradiation. After the sample is activated, the degree of care can be relaxed since the sample is easily differentiated from any contamination, other than radioactive, which might be introduced. The insensitivity to handling procedures after irradiation is one of the most attractive features of activation analysis. In order to maximize this advantage, preirradiation handling should be held to a minimum.

If possible, the sample should be transferred from its irradiation container into a counting container, as this will eliminate the problem of subtracting the trace-element content of the irradiation container. If the sample is to be counted in its irradiation container or with a binder, the trace-element content must be well known from previous analyses of a statistically significant number of containers or specimens of binder. The same clean handling techniques must be applied to the container or binder.

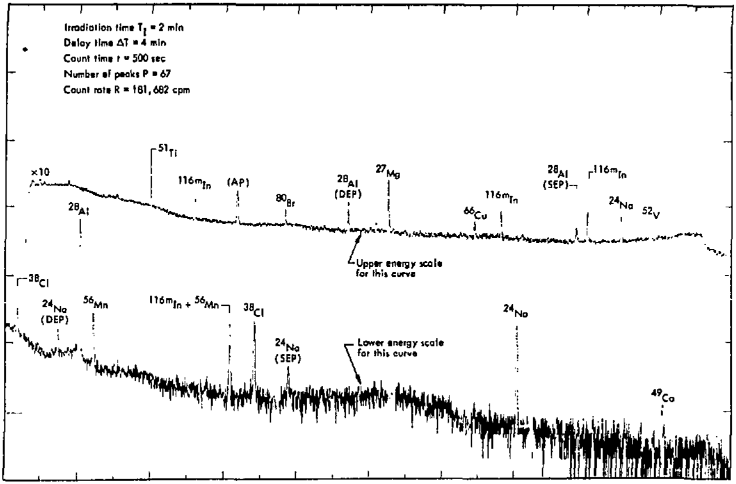

Fig. 4 INAA spectrum Q1 for high-volume air filter sample IAS-21A. Sample data: total airflow through filter 958 m^3; mass loading of air as indicated by material trapped in filter, 226 $\mu g/m^3$. SEP = single escape peak; DEP = double escape peak; AP = annihilation peak.

Samples may be either in solid or liquid form, the solid being preferred. In general, liquid samples may require a concentration step before irradiation. In the case of liquids such as milk, the sample is brought to a solid form by freeze-drying.

Sample Geometry

The question of geometry must be considered in two aspects, irradiation and counting. In some cases, the same geometry will apply to both situations, namely when the disk shape, which is ideal for counting, can be irradiated. When the sample cannot be irradiated in disk form, it may be possible to approximate such a geometry during counting by packaging a powdered sample in a flat polyethylene envelope, or a liquid in a cylindrical vial.

Techniques have been worked out for preparing most dry samples in the disk shape for irradiation. The basis of these techniques is the use of a hydraulic press and appropriate dies. Some samples, such as freeze-dried skim milk, will maintain their shape after pressing while others require the addition of some binder material. If a binder is used, it must be treated as any other trace-element content introduced into the sample.

In all cases, whether the sample is in a form for counting or not, each sample is accompanied by a flux monitor foil

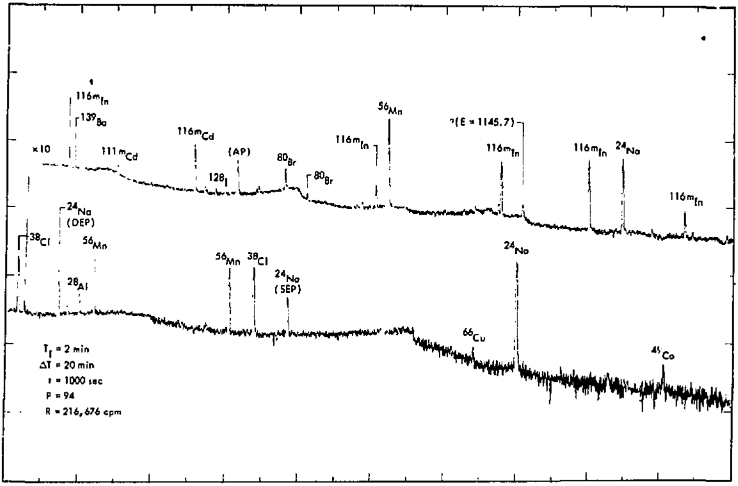

Fig. 5 INAA spectrum Q2 for high-volume air filter sample IAS-21A. (Sample data and abbreviations same as Fig. 4.)

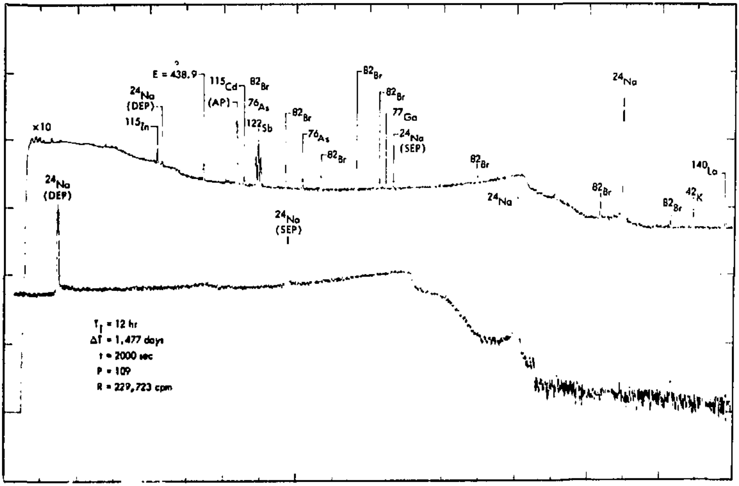

Fig. 6 INAA spectrum L1 for high-volume air filter sample IAS-21A. (Sample data and abbreviations same as Fig. 4.)

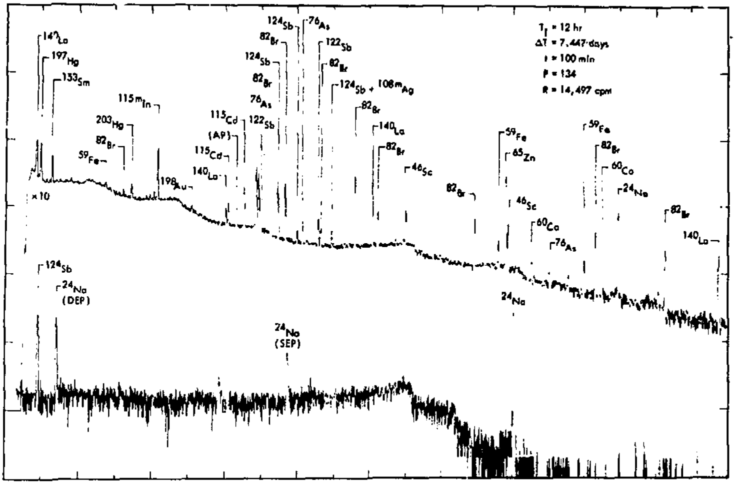

Fig. 7 INAA spectrum L2 for high-volume air filter sample IAS-21A. (Sample data and abbreviations same as Fig. 4.)

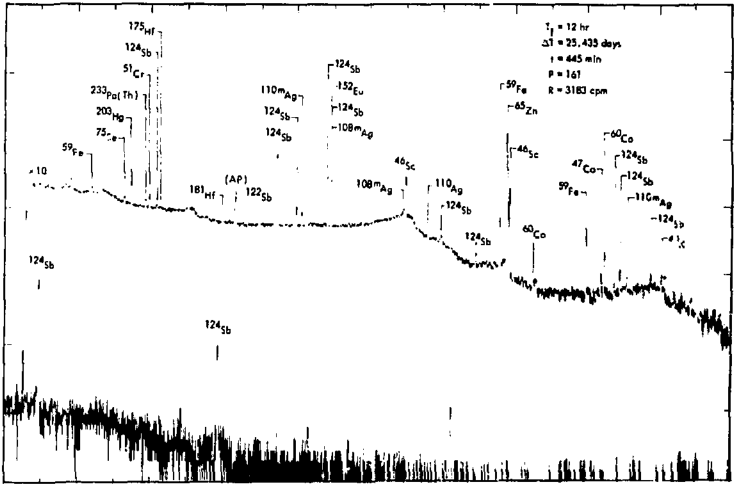

Fig. 8 INAA spectrum L3 for high-volume air filter sample IAS-21A. (Sample data and abbreviations same as Fig. 4.)

during irradiation. Each foil is counted separately and enables us to normalize for flux variations between samples and standards.

Liquid Samples

When a sample must be irradiated in liquid form, several precautions must be observed. Basically the problem is that of leakage of the sample from its container. It can be assumed that there will be a build-up of pressure due to heating and radiolysis. It is necessary to provide some space in the container for such a release of gas. About one-half to two-thirds of the volume of the container should be available for expansion. The sample must be sealed in its container by welding, in the case of plastic vials, or heat sealing for quartz. The heat-sealed primary container must then be contained in a leak-proof outer container. The LPTR user guide[4] provides physical dimensions of most available outer containers.

After irradiation, the container is opened, and the liquid is transferred to a counting vial. It is possible to count the sample in the irradiation container if counting geometry and container blank are taken into consideration.

Solid Samples

Solid samples have a number of advantages over liquid. The most important of these is the absence of leakage consideration and the consequent relaxation of sealing requirements. These samples must still be held in a primary container which is closed tightly, but not necessarily sealed. There must be a secondary container as in the case of liquids.

Another advantage is the ease of handling and the consequent reduction of exposure of personnel to radiation. As stated before, the solid sample may be pressed into a disk shape. The disks are made in a variety of diameters, ranging from a quarter-inch to one inch. If binder is necessery, a weighed quantity is added to the weighed sample. Powdered polyethylene and Avicel are two commercially used binders. The polyethylene requires heating to form the wafer and does not require much pressure. The Avicel requires no heat, but more pressure. Both materials have acceptable blanks for most samples.

Among solid samples we must include samples of suspended particles in air or other gases. Such particles are generally collected on the collection media. The blank for the collection media must be determined as for other cases.

Sample Size

The sizes of samples varies with the type of sample, the matrix, and the information desired. Experimental conditions often determine sample size. For example, air sampling is limited by low concentrations of aerosol, sampling time, and collection media capacity. In other cases, enough sample might be available to produce any size desired, such as with milk, coal, soil, etc. The limiting factors are then the amount of radiation from the major constituents which can be handled and counted, and the mixture of major and trace elements.

The range of sample sizes used in analyzing most solids is from 1.0 mg to 1.0 g. Liquids can be handled in amounts up to about 30 ml.

Validation

For the determination of the overall accuracy of the use of INAA, we have access to three different types of verifications. The first of these verifications is to analyze some standard material and compare our measured values to those certified by the agency issuing the standard. In our case, we analyze orchard leaves as certified by the National Bureau of Standards.

The second approach is 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, is the possibility of intercomparison within an experimental program. This involves a direct comparison of the elements determined to be in the same sample by different analytical techniques, and a comparison of an overall view of data produced by different techniques, not necessarily looking at the same elements.

NBS ORCHARD LEAVES

Samples of NBS standard reference material — orchard leaves (SRM-1571) — have been analyzed. The values shown in Table 6 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.

Table 6. National Bureau of Standards SRM-1571 Orchard leaves (μg/g)

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

EPA-NBS INTERCOMPARISON SAMPLES OF COAL DUST AND FLY ASH

A "round-robin" intercomparison study was sponsored jointly by the National Bureau of Standards and the Environmental Protection Agency. The proposed standards were coal (SRM-1632), fly ash (SRM-1633), gasoline, and fuel oil. LLL participated in the measurements of coal dust and fly ash.

Tables 7 and 8 show the reported results.[8]

Table 7. NBS-EPA fly ash (SRM-1633) comparison

μg/g (unless indicated)

	U. of Md.	NBS[a]	Battelle N.W.	Livermore	Washington State	Oak Ridge
Na	0.34% ± 0.03%		0.37% ± 0.02%	0.28% ± 0.02%		0.34%
K				1.38% ± 0.06%		2.54%
Ca	4.2 % ± 0.5 %			4.48% ± 0.26%		2.94%
Ba	0.27% ± 0.03%		0.34 ± 0.04	0.26% ± 0.02%		0.276%
Al	15.8 % ± 1.2 %		12.6 % ± 0.4 %	12.3 % ± 0.6 %		8.74%
Sc	27 ± 1.5		27 ± 1.0	28.0 ± 1.7		35.1
Ti	0.73% ± 0.04%		0.76 ± 0.0	0.72 ± 0.07		0.588%
V	251 ± 26	214 ± 8	220 ± 15	244 ± 24	223.6 ± 12.3	170
Cr	130 ± 5	132 ± 5	131 ± 8	126 ± 10	126.2 ± 4.3	
Mn	509 ± 15	495 ± 30	489 ± 11	506 ± 23	480 ± 10.1	441
Fe	6.2 % ± 0.3 %		6.51% ± 0.31%	5.8 % ± 0.3 %		
Co	41.2 ± 1.0	38[b]	40 ± 2	42 ± 1.9		
As	59.6 ± 1.0	61 ± 3		51.7 ± 3.3	78.7 ± 3.6	
Sb	7.8 ± 1.5		7.2 ± 0.8	6.38 ± 0.41		7.84 ±
In				0.32 ± 0.10		
Hf	7.9 ± 0.6		8.2 ± 0.8	5.79 ± 0.38		
Ta	1.64 ± 0.12		3.5 ± 0.3			
W				3.5 ± 1.1		
La	82 ± 5		82 ± 4	65.0 ± 6.6		82.1
Ce	156 ± 12			135 ± 7		
Sm	13.8 ± 0.6		12.4 ± 0.5	11.1 ± 0.7		
Eu	2.9 ± 0.2		2.3 ± 0.1	2.22 ± 0.20		
Th	23.5 ± 2.0	24[b]	26.2 ± 1.3	23.3 ± 1.3		

[a] Probable certified value, unless otherwise indicated.

[b] Informational value only.

Table 8. NBS-EPA coal (SRM-1632) comparison

μg/g (unless indicated)

	U. of Md.	NBS[a]	Battelle N.W.	Livermore	Washington State	Oak Ridge
Na	339 ± 20		420 ± 30	313 ± 22		479
K				0.23 ± 0.01		0.385%
Ca	0.41% ± 0.05%			0.42% ± 0.07%		0.268%
Ba	330 ± 30			327 ± 19		317
Cl	970 ± 110		800 ± 200	758 ± 62		652.6
Br	~20			18.6 ± 2.4		16.0
Al	1.78% ± 0.16%		1.78% ± 0.08%	2.0 % ± 0.1 %		1.23%
Sc	3.70 ± 0.25		3.4 ± 0.3	3.94 ± 0.19		6.06
Ti	960 ± 100		1110 ± 200	1060 ± 120		789
V	37.0 ± 3.3	35 ± 4	33.0 ± 4	38.3 ± 3.3	36 ± 3.8	26.4
Cr	19.7 ± 1.0	22 ± 2	19 ± 2	19.3 ± 0.97	21.25 ± 0.43	
Mn	45.2 ± 3.2	47 ± 3	41 ± 6	47.6 ± 3.4		38.6
Fe	0.86% ± 0.06%	0.80%[b]	0.82% ± 0.07%	0.81% ± 0.04%		
Co	5.6 ± 0.3		5.2 ± 0.4	6.04 ± 0.28		
Zn	~30		37 ± 4			
As	5.7 ± 0.5	5.9±0.4		5.04 ± 0.66	11.23 ± 0.33	
Sb	4.3 ± 3.0		3.7 ± 2.0	4.1 ± 5.3		4.4
In				0.20 ± 0.12		
Hf	0.95 ± 0.08		0.97 ± 0.1	0.72 ± 0.06		
W				0.62 ± 0.27		
La	11.3 ± 0.6		10.5 ± 0.5	9.1 ± 0.38		12.8
Ce	20.4 ± 1.5			18.5 ± 0.65		
Sm	1.83 ± 0.09		1.7 ± 0.3	1.43 ± 0.07		
Eu	0.38 ± 0.03		0.28 ± 0.01	0.32 ± 0.01		
Th	3.0 ± 0.3	3[b]	3.45 ± 0.18	2.97 ± 0.17		
U						1.26

[a] Probable certified value, unless otherwise indicated.

[b] Informational value only.

INTERLABORATORY COMPARISON OF STANDARD SAMPLES

A comparison of trace element concentrations determined by 5 different nondispersive x-ray fluorescence techniques used at 11 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 four of Table 9.

Each set of data reported in Table 9 was from 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 amounts ranging from 1.7 $\mu g/cm^2$ to 54 $\mu g/cm^2$. All investigators received separate sets of standards. *LLL* used the *same set* for x-ray analysis prior to INAA.

The gravimetric standard solutions deposited on Whatman 41 are referred to as "A" and "C". The values shown for each element in Table 9 are ratios of the 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.

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*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.

Applications

TRACE ELEMENTS IN AEROSOLS

The California Aerosol Characterization Experiment (ACHEX) 1972-1974

Some of the more pressing questions of air pollution requiring improved knowledge are those dealing with aerosols. Although airborne particles represent a small fraction of the trace constituent loading in air, they contribute significantly to environmental degradation as a potential hazard to health, a visibility reducer, and a possible agent of weather modification. Despite many years of investigation, the origins and evolution of atmospheric aerosols remain poorly understood quantitatively, compared with trace gases. Recognizing this, the California Air Resources Board (ARB) sponsored a major experiment in air chemistry, devoted to a detailed study of aerosols in urban and remote sites of California.[2]

As the objectives note, the project was set up in such a way as to emphasize

Table 9. First XRFA intercomparison study

Ratio of A and C averages to gravimetric standards

Set no.	Sample type	Al	K	V	Mn	Fe	Cu	As	Pb
1	A		0.09(.21)	0.76(.06)	0.64(.06)	0.57(.20)	0.53(.08)	0.48(.07)	0.57(.07)
	C		0.73(.24)	0.68(.10)	0.68(.08)	0.65(.10)	0.60(.10)	*0.69(.08)*	*0.74(.09)*
2	A	1.73	0.67	0.72	0.76	0.67	0.79	0.61	0.69
	C		0.91	0.77	0.83	0.74	0.76	0.63	0.69
3	A		0.92(.07)	0.91(.07)	0.95(.07)	0.91(.03)	0.92(.04)	0.90(.04)	0.94(.03)
	C		0.91(.06)	0.90(.06)	0.92(.04)	0.89(.04)	0.91(.03)	0.89(.03)	0.88(.03)
LLL	A	0.79(.01)		0.91(.01)	0.94(.02)	0.84(.01)	0.89(.19)		
INAA	C	0.79(.08)		0.89(.01)	0.96(.02)	0.83(.02)	1.20(.19)		
5	A		0.82(.02)	1.01(.02)	0.99(.03)	0.92(.02)	1.00(.03)	0.94(.03)	1.05(.03)
	C		0.81(.03)	0.97(.03)	0.95(.03)	0.91(.03)	0.96(.03)	0.94(.03)	0.99(.03)
6	A	1.55(.20)	0.94(.01)	0.92(.01)	1.01(.02)	1.01(.01)	0.91(.03)	0.76(.07)	0.98(.05)
	C	2.51(.37)	1.01(.01)	1.04(.01)	0.95(.02)	0.96(.01)	0.88(.02)	1.20(.08)	0.92(.03)
7	A	1.36(.12)	0.95(.06)	0.90(.06)	1.10(.07)	1.00(.05)	0.92(.04)	0.86(.06)	1.00(.05)
	C	1.78(.11)	1.15(.07)	1.12(.08)	1.17(.08)	1.06(.04)	1.07(.06)	0.88(.05)	1.01(.05)
8	A		1.06(.16)	1.01(.15)	1.12(.17)	1.11(.17)	0.97(.16)	1.03(.15)	0.96(.15)
	C		1.03(.15)	1.07(.16)	1.02(.15)	1.09(.16)	1.11(.17)	1.15(.17)	1.06(.16)
9	A			0.86	0.90	0.98	1.01	1.00	1.03
	C			1.04	1.10	1.16	1.17	1.11	
10	A	1.66(.25)	1.28(.18)	1.15(.17)	1.21(.19)	.93(.13)	.74(.23)	1.10(.25)	1.13(.27)
	C	*1.76(.26)*	*1.25(.20)*	*0.91(.14)*	*1.11(.18)*	*.86(.12)*	*.86(.10)*	*1.05(.24)*	*1.09(.24)*
11	A	0.71	0.92(.06)	1.10(.06)	1.03(.08)	1.01(.08)	0.88(.09)	0.93(.12)	0.84(.08)
	C	0.58	0.92(.06)	1.17(.09)	1.09(.08)	1.09(.08)	0.92(.07)	1.06(.17)	0.81(.09)
12	A	6.5 (2.1)	1.13(.18)	0.99(.07)	1.01(.09)	1.01(.11)	1.01(.12)	1.08(.15)	1.04(.10)
	C	5.0 (1.3)	1.18(.15)	1.02(.10)	1.06(.12)	1.11(.12)	1.04(.10)	1.18(.16)	1.07(.11)

primary particle sources, atmospheric formation, and their relation to changes in visibility. In California, the "secondary" production of aerosols by chemical and physical processes in the atmosphere is believed to be especially important.

The objectives of the study to which INAA were applied were:

1) To characterize the aerosol in the South Coast, the San Francisco Bay Area, and the San Joaquin Valley Basins, in terms of its interaction in the atmosphere, and its natural and anthropogenic origins.
2) To evaluate the amount of the atmospheric aerosol in the cited three major air basins which can be related to: (a) primary emissions, such as from auto exhausts or smokestacks, and (b) secondary production, due to physical and chemical processes taking place in the atmosphere.
3) To identify those major sources of particles which can be related to aerosol pollution and visibility reduction.
4) To evaluate the applicability of the aerosol analysis instrumentation employed in this study for use in present monitoring networks.

The results of the experiment revealed an extremely complicated behavior of atmospheric aerosols, as they are influenced by local sources, gas-particle interaction, and meteorological factors. However, certain important common features of airborne particles were found. For instance, the effort showed clearly that man's activities and atmospheric transformations of gaseous pollutants contribute primarily to the submicron particle size range, while primary natural sources influence the range > 1 μm diameter.

Approximately 700 filter and impactor samples were analyzed during the study. Total aerosol specimens were collected on 5 μm cellulose acetate membrane filters using low-volume air samplers. Multistage rotating drum cascade impactors were used to collect size-segregated aerosols. The particle-size distributions obtained had 50% cut points of 8.0, 4.0, 1.5, and 0.5 μm. Cellulose acetate after-filters collected particles > 0.5 μm.

The aerosol specimens were routinely analyzed for Na, Mg, Al, Cl, Ca, Ti, V, Mn, Cu, Br, In, I, and Ba using a 2-minute irradiation at 3-Megawatts in the LPTR followed by 9 and 20-minute counts (Table 1). Sensitivities obtained for 10 of the elements were routinely less than 10 ng/cm^3. Selected samples were further analyzed for Eu, Ce, Se, Th, Cr, Hf, Ag, Ni, Sc, Fe, Zn, and Co, using a 12-hour irradiation followed by an 800-minute count after a 3-week decay.

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 appear strongly in the submicron (or anthropogenic) fraction. Examples included Br, Cl, and V. In the supermicron fraction appear the natural or quasinatural elements such as Na, Cl, Al, Fe, Ca, and Sc. 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.

Aluminum was found principally in the larger particles (8-15 μm) at all urban, inland, and coastal sites. Since large particles are usually a result of wind-blown soil erosion, the Al concentrations were used as indicators of the amount of soil component in the aerosols. Other elements with Al-like distributions were Ca, Mg, Mn, Sc, Th, Fe, and Co, implying they were also soil-derived. The V distributions were bimodal with maxima at submicron ranges (< 0.5 μm) and large particle-sizes (> 8.0 μm). These data suggest two sources of V, soil dust and combustion (probably the burning of residual fuel oil) processes.

The Na at coastal sites was from sea-salt and present in the 1.5 - 4.0 μm particle size range. The Na at inland sites was derived from soil-erosion and found in the large-particle range, 8-15 μm. At coastal sites the Cl distribution followed the Na distribution. At inland sites the submicron Cl (as well as the Br), which was due to automotive emissions, increased significantly.

A secondary, but important 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 stage 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. These techniques have been summerized in Ref. 10.

Air Sampling in the Vicinity of Smelting Operations

An example of what can be accomplished in aerosol characterization is shown by a study of air filter samples collected at Kellogg, Idaho,[1] in the Coeur d'Alene mining district. Samples were analyzed to determine the concentrations of trace metallic elements in the air, and to look for indications of their sources. For example, some elements are in the air as a result of the mining and smelting operations, others are there "naturally" through being picked up by the winds from the soil surfaces.

The samples were analyzed for 34 elements with instrumental neutron activation analysis, and for 6 elements with x-ray fluorescence analysis. The elements observed were divided into three main groups according to their enrichment factors (defined as enrichment of the element concentration relative to the worldwide average concentration in the earth's crustal rock). The elements with low enrichment factors (<100), were considered to be derived primarily from the soil. Those with an intermediate enrichment factor (100 to 1000) are considered to be of uncertain origin (soil and/or mining and smelting). Those with a high enrichment factor (>1000), are considered to be clearly of mining/smelting origin.

From a cursory examination of Figs. 9a - 9g one may draw several conclusions as to the possible sources of some of the possible sources of some of the elements.

From Figs. 9a & b we can see that Pb, Zn, Cd, In, and possibly Ag, Au, Se, Sb, and Hg have similar concentration patterns as a function of time. However, they are not correlated with the behavior of the total mass of the sample. From Figs. 9c & d we see several elements that tend to have a distribution similar to that of Al. In Fig. 9e, 9f, & 9g we observe elements that do not appear to be very well related to either the Pb or Al distribution. From the observation of the data in Figs. 9a - 9g, one would conclude that the elements can be grouped into three general classes: (1) those with a pattern similar to that of lead, probably associated with the mining or smelting industry; (2) those with a pattern similar to that of Al and therefore probably related to the soil; and (3) those that do not seem to fall into either of the first two classes.

The relationship between the results of XRFA and INAA is shown in Fig. 10 for Cu, Br, Fe, and Zn. The solid line represents a correlation coefficient of 1.0, or perfect correlation. The linear correlation coefficients of these four elements are 0.98, 0.96, 0.93, and 0.97, respectively. for Cu, Br, Fe, and Zn. For these samples a linear correlation coefficient of 0.35 is the minimum value for correlation.

Soil and Vegetation Trace Metal Contamination Near Zinc and Lead Smelters

Soil cores and vegetation samples were taken at 12 sites in the vicinity of Zn and Pb smelters in Kellogg, Idaho.[11] Thirty-four elements were analyzed using the techniques of Instrumental Neutron Activation Analysis and x-ray fluorescence analysis. The soild and vegetation were found to be highly contaminated with Pb, Zn, Cd, As, Hg, Se, Sb, Ag, and In. These same elements had been found at high concentrations in ambient air aerosols collected in Kellogg two miles from the smelters. In the surface soil fraction the concentrations were 170 to 7900 ppm Pb, 220 to 13000 ppm Zn, and 18 to 140 ppm Cd. In the vegetation the concentrations were 220 to 10000 ppm Pb, 450 to 12000 ppm Zn, and 16 to 950 ppm Cd. The aerosol enrichment factors relative to the mean surface soil concentrations were 4100 for Cd, 180 for As, 110 for Pb, and 60 for Zn.

UPTAKE OF TRACE METALS BY VEGETABLES GROWN IN LIVERMORE TREATMENT PLANT SLUDGE

The Laboratory routinely releases small quantities of trace elements and radionuclides into the Livermore sewer system, in accordance with appropriate standards. At the Livermore Waste Water Treatment Plant these tend to separate with the digested sludge. This sludge is available to the public for use as a soil conditioner. A study[3] was conducted at LLL during 1974 to determine the uptake of these elements by edible crops grown in soil treated with sludge.

Sludge was applied 7 cm thick to an experimental garden plot 10 m by 15 m. Soil was mixed to 14 cm with a rototiller, giving a 50% sludge mix. A control plot of similar dimensions but with no added soil conditioner or fertilizer was also established. A variety of plants and seeds were planted that would produce root, stem,

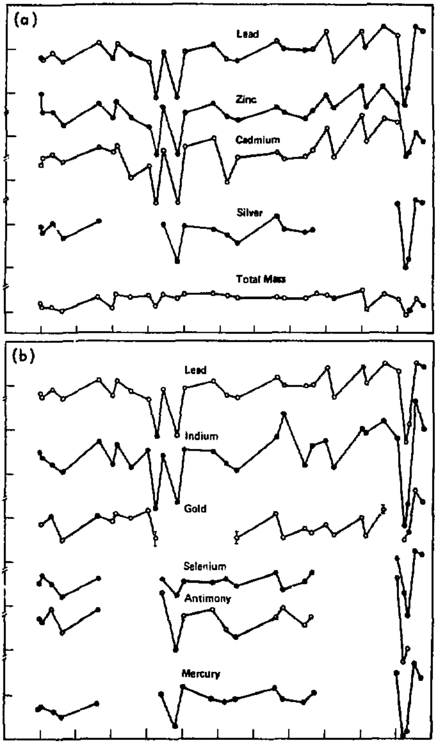
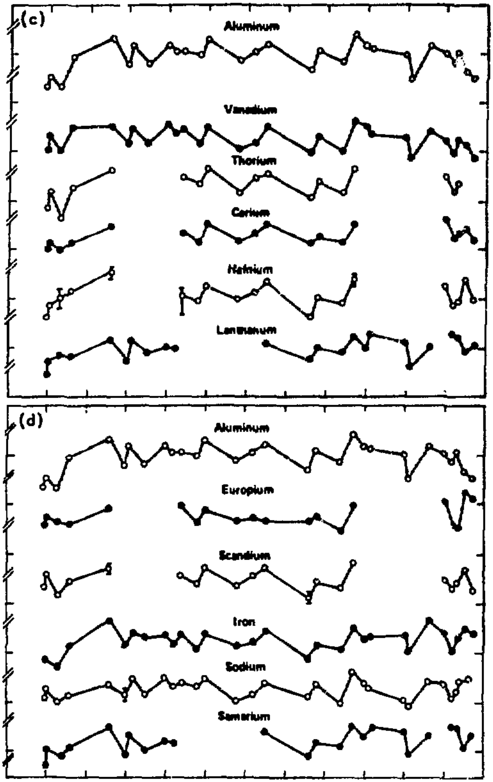
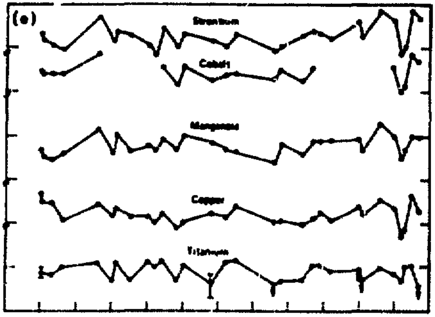
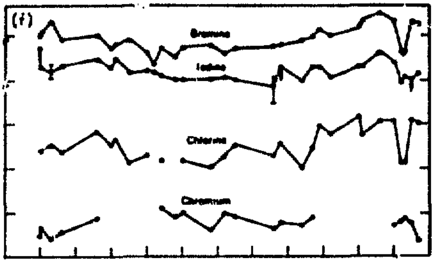
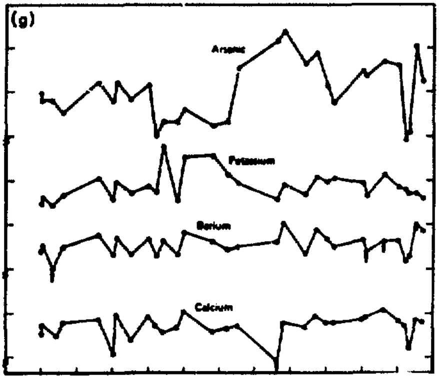


Fig. 9a-g Concentration of various trace elements in the air as a function of sampling date, for air filter samples taken in Kellogg, Idaho, 1972.


(c)
Aluminum
Vanadium
Thorium
Cerium
Hafnium
Lanthanum
(d)
Aluminum
Europium
Scandium
Iron
Sodium
Samarium


(e)
Strontium
Cobalt
Manganese
Copper
Titanium


(f)
Bromine
Iodine
Chlorine
Chromium


(g)
Arsenic
Potassium
Barium
Calcium

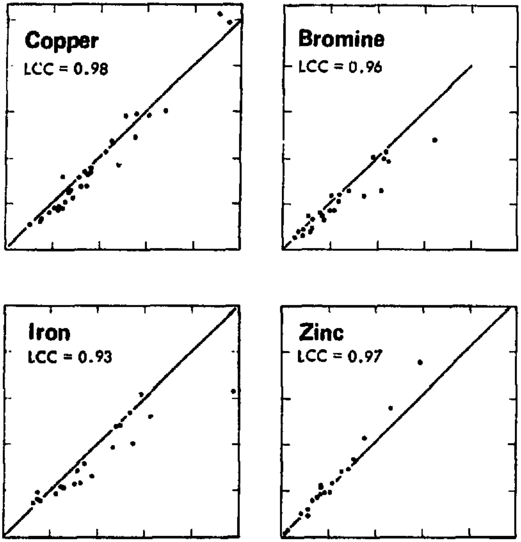


Fig. 10 Correlation of INAA and XRFA results for Cu, Br, Fe, and Zn. Linear correlation coefficient (LCC) values are shown: a value of 0.35 or higher indicates a positive correlation.

leaf, flower, fruit, and seed parts that could be analyzed for uptake of the several elements of interest.

Trace-element content was determined principally by atomic absorption and neutron activation.

Principal Findings

Zinc and cadmium levels in the sludge soil were 15 to 75 times higher than those in the control soil. Freeze-dried lettuce and radish leaves from plants grown in sludge soils contained Zn and Cd levels equal to those in the soil. Although the Sn levels in the sludge soil and control soil were about equal, Sn uptake was much higher in control-grown plants than in those grown in the sludge garden. The Ca content of the sludge soil was higher than in the control, and the plants may have reached their capacity for divalent alkaline earth ions with Ca. Copper levels in the sludge soil were 20 times higher than in the control soil, but plants grown in the sludge soil showed no higher Cu uptake. Chromium uptake was also negligible. Finally, seeds showed very little concentration of trace elements, while leaves generally were quite responsive to change in trace metal content of the soil.

INAA OF MARINE SAMPLES DEVELOPED IN THE MARINE STUDIES PROGRAM

In coastal regions, reactors located on the coast can use sea water for cooling and for disposing of low level radioactive wastes. The Biomedical and Environmental Research Division had undertaken a coastal studies program whose purpose was to investigate the fate of radionuclides released into a marine environment. One phase of the program involved the study[12] of the Pacific Cas and Electric Company reactor at Humbolt Bay, where over a three year period all reactor releases were assayed for radionuclide composition and concentration and the uptake of the radionuclides by sediments and biota was followed. Stable element concentrations in the various environmental compartments were determined by neutron activation analysis. We want to know the concentration in each compartment of the stable element counterpart for each of the radionuclides released in order to understand the observed radionuclide partitioning. Thus, if we know that in a particular aqueous pool the ratio of radioactive ^{65}Zn to stable Zn is 0.3 pCi/µg; and if we know that mature oysters have stable Zn concentrations of 4000 µg Zn/kg wet weight of oyster, then we expect the concentration of radioactive ^{65}Zn in the oysters to reach .3×4000 or 1200 pCi/kg wet weight.

Elements of interest in the coastal studies program are those having a radioactive counterpart which is released into the marine environment. Since these are all relatively long-lived species produced by neutron capture, the method of Instrumental Neutron Activation Analysis for determining these elements is particularly appropriate. Elements required for the Humbolt Bay study were Cs, Ce, Mn, Zn, and Co. These were determined for three main catagories of sample — seawater, sediment, and biota. Seawater samples were filtered and acidified at the point of collection. At the laboratory, the trace elements from four liter samples were preconcentrated, first by evaporation to reduce water volume by a factor of four, and second by selectively precipitating elements of interest to eliminate sodium which in seawater is a major interference. The ashed precipitates were irradiated for eight hours, cooled for one week, and counted to determine the quantity of the activation products.

Sediment samples were dried and then 100 mg aliquots were irradiated, cooled, and counted using the same schedule as above. This schedule was also followed for the biota samples. In this case, however, the original biological material was first dried and then ashed at 450°C to provide a 100 mg sample.

In all cases, additional elements were routinely determined by the analysis. These included Sc, U, Th, Cr, Nd, Mo, Fe, Sm, Ag, Rb, and Eu; although not every one of these elements was determined on every type of sample.

FORENSIC ANALYSIS

An area currently being investigated is forensic analysis. There is an increasing need to provide scientific support to law enforcement groups to aid in the resolution of criminal cases. A very practical and valuable test is one for gunshot residue determination. The results of the test indicate whether it is likely that a suspect has fired a gun. This is done by analyzing swipes from the suspect's hands for antimony and barium traces. If the suspect has fired a gun, traces of antimony and barium will probably be deposited as residues from the dispersal of powder from the bullet primer.

Trace element analysis can provide valuable information in many other ways. Hair trace analysis can be used for indication of arsenic poisoning. Analysis of hair, paint, glass, fibers, oil, rubber and miscellaneous materials can be used to connect a suspect to a crime.

Another important area in law enforcement is the ability to tag items so that positive identification can be made at a later time. Some applications are: tagging items to be sold by an undercover agent to a known fence, or introduced into the chain of a smuggling operation. Eventually an arrest is made, and if the items can be traced to the source, it can be valuable information for obtaining a conviction. We have tagged over 175 items for the U.S. Customs Service, and some have been recovered and identified. This information has been used as major evidence in two felony court cases.[13]

Conventional methods, such as tagging with dyes that will show up under black light, are becoming less effective as the criminals become more sophisticated. For that reason, new tagging methods are required. Three methods we have worked with are: vacuum deposition of rare earth elements, affixing uniquely-coded microspheres, and evaporation of a rare earth mixture solution. Other methods under consideration are diffusion and ion implantation. In all of these methods, a known ratio of rare earth elements are affixed in some way to an object such as an item of jewelry. If the item is lost or stolen and later recovered, the tag can be detected and provide a positive means of identification. Detection can be accomplished by Instrumental Neutron Activation Analysis.

There are many other uses for positive identification marking methods. Thefts from the docks and shipping losses are an ever increasing problem. Insurance companies and trade protective associations as well as law enforcement agencies could use and benefit from such positive identification methods. With the development and application of these techniques, a fence will no longer be able to buy stolen goods and feel secure that the item is not identifiable as stolen property.

TRACE ELEMENTS IN MILK

The role of trace elements in the environment both as toxic materials and as essential nutrients for plants, animals, and man is well recognized. However, except for a few notable examples, very little information is available on the presence and flux of these elements through the biosphere and into human food chains. With the presently increasing concern over energy-related trace element pollution, it becomes most appropriate to undertake a comprehensive study of trace elements in major food chains by modern instrumental methods of multi-elemental analysis. This documentation is of value both in itself and in improving the understanding of radionuclide behavior in the environment.

The specific objectives of the LLL *soil-forage-cow-milk food* chain study are:

1. To document trace-element levels in each compartment of this food chain to permit broad interpretations of the relationship between trace elements in milk, soil characteristics, climate, dairy management practices, and industrial pollution;
2. To evaluate the usefulness of milk as an indicator of trace-element pollution in the environment and to establish baseline levels of contamination;
3. To develop methods and models for future systematic investigations of other food chains and other materials.

All trace elements detectable by the multi-elemental analytical techniques will be reported, but particular emphasis will be placed upon those known or suspected of being toxic or essential. The results will be data-banked and evaluated for statistically significant correlations.

The results of the first pilot phase of this study, which is a survey of trace elements in market milk collected in California and Colorado, have been reported in Ref. 14. This survey served as a focus for developing procedures for the assay of trace elements using Instrumental Neutron Activation and x-ray fluorescence techniques. Intercomparisons between the two techniques were carried out as a validation of the analytical procedures. Collection procedures were also tested and validated during the course of the study.

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