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ABSTRACT

Title of Thesis : The Quantitative Analysis of Airborne Particulates by X-Ray Fluorescence.

George C. Asteriou, Masters of Engineering Science, 1984

Thesis directed by : Dr. Barbara Kebbekus

Airborne particulate matter from the New Jersey State area collected on Quartz Microfiber filters was analyzed by X-Ray Fluorescence spectroscopy. The quantitative analysis of the samples against N.B.S. standards produced results which were compared with Atomic Absorption analysis.

The results from the two methods were correlated by the introduction of empirical factors for each element.

However, a larger number of analyzed standards of varied composition, along with the creation of a spectral library, can minimize the need for empirical factors and yield accurate results.

THE QUANTITATIVE ANALYSIS OF AIRBORNE PARTICULATES BY X-RAY FLUORESCENCE

By

GEORGE C. ASTERIOU

Thesis submitted to the Faculty of the Graduate School of the New Jersey Institute of Technology in partial fulfillment of the requirements for the degree of Master of Science in Engineering Science.

FALL 1984

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TABLE OF CONTENTS

SECTION		PAGE
1.	Introduction	1
2.	History and Background	3
3.	Method's Objective	15
4.	Instrumentation	18
5.	Preparation of Analysis and Selection of Conditions	22
6.	XRF Data Acquisition	29
7.	Analysis by AA	70
8.	Results and Statistics	75
9.	Discussion	99
10.	Conclusion	102
	References	103

LIST OF TABLES

TABLES		PAGE
I.	X-Ray Notation for the Subshells of the K, L, M and N Shells.........	11
II.	Analytical Techniques and Parameters..........................	17
III.	X-Ray Emission Lines................	22
IV.	List of Excitation Conditions.......	27
V.	Certified Concentration Values of N.B.S..............................	28
VI.	Results of XRF Analysis.............	68
VII.	Conditions for AA Analysis..........	70
VIII.	Data for AA Sample Analysis.........	71
IX.	Results of AA Analysis..............	73
X.	Ratio and Statistics for AA and XRF.	75
XI.	Factors for each Element............	79
XII to XX.	Final Results For each Element......	81-98
XXI .	Summary of Comparison...............	101

LIST OF FIGURES

FIGURES		PAGE
1.	Atomic Shells.....................	5
2.	Production of K, L, and M X-Rays..	5
3.	K X-Ray Transitions...............	9
4.	Energy Level Diagram..............	13
5.	Diagram of the Quantex-Ray System.	19
6 to 34	Quantex-Ray Graphics..............	32 to 60
35.	NBS Quantex-Ray Graphics..........	62
36	Blank Background Quantex-Ray Graphics.........................	65

1. INTRODUCTION

Progress in environmental chemisty and all related areas of materials research in the past three decades has been greatly affected by the introduction of new methods, techniques, and instruments, some of which are highly sophisticated. With the rise in general awarness of the effects of trace chemicals in the environment on mans health, it has been realized that traditional methods of analysis are often inadequate. The growing realization of the importance of even extremely small amounts of metals in the environment has led to an increasing demand for determination of these metals at trace level concentrations. The resulting flood of data has evoked a mixed response from members of the public, scientific and otherwise. Some accept the results without hesitation and make them the basis for legislative action, while others indicate that it is the vast progress of analytical techniques and instruments that can make possible such measurements. In either case to safeguard the quality of the air we breathe it is necessary to continue the development of improved analytical methods for identification.

characterization, and measurement of pollutants in the ambient atmosphere.

X-ray fluorescence (XRF) spectroscopy has proved to be one of the more successful methods for monitoring the concentrations of trace elements in the environment. (11, 12, 13). The major advantages of the XRF method are its high precision, the capability of simultaneous multielement analysis, and the convenience of preparation free samples.

The primary topics of this thesis are : (1) the capability of the XRF method to produce quantitative results, (2) the reliability of these results compared with Atomic Absorption analysis, and (3) the ability to reproduce these results by creating common standards for the two methods.

2. HISTORY AND BACKGROUND

A. X-RAYS

X-rays are a type of electromagnetic radiation. The x-ray region of the electromagnetic spectrum is, approximately, the region between 0.05 and 125 kilo-electron volts (KeV). One electron volt is defined as the energy acquired by a particle that has one unit of electrical charge (the charge of a single electron) after it has passed through an electrical potential difference of one volt. One electron volt is equal to 1.602×10^{-19} joules. (A thousand electron volts are equivalent to a kilo-electron volt.)

X-rays are produced by the bombardment of a target by fast moving electrons in partial vacuum. William Conrad Roentgen first discovered this fact in 1895 while he was experimenting with a cathode tube. He found that when the cathode ray tube was operating, it produced fluorescence in a platinum-barium cyanide screen that happened to be nearby. The source of the mysterious rays that caused this fluorescence was found to be the glass walls of the cathode ray tube. It was determined that these "X" rays were caused by the electrons

being emitted from the cathode of the tube after they struck its glass walls. (8).

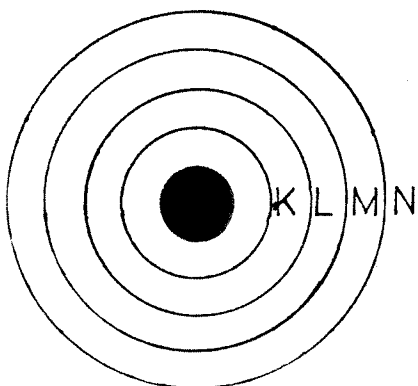
The x-ray tube is an adaption of the cathode tube used by Roentgen. However, instead of allowing the electrons to bombard the glass walls of the tube they are focused onto a metal target. This target intercepts the electrons from the cathode and emits x-rays. Since the target material of the x-ray tube is known, the energies of the emitted x-rays are predictable because they are characteristic of the elements in the target. (2).

When the cathode filament is heated to incandescence (glowing white hot) by an applied current, it emits electrons. The electrons are accelerated to the target by the potential difference (voltage) in the tube between the cathode (-) and the anode (+). The energy of the accelerated electrons in KV depends upon the magnitude of the difference in potential between the cathode and the anode. When the electrons hit the anode they produce x-rays. (5).

B. ATOMIC STRUCTURE AND EXCITATION.

The Bohr model of the stucture of an atom is shown in figure (1). At the center of this atom is the nucleus, surrounded by electrons that travel in different shells

Fig. (1). ATOMIC SHELLS.



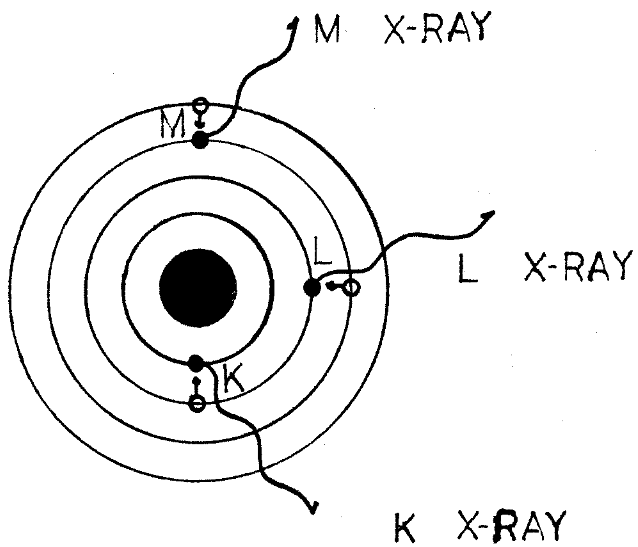


Fig. (2). PRODUCTION OF K, L, AND M

X-RAYS.

around it. These shells correspond to the energy levels of the electrons in them. The shell closest to the nucleus is called the "K" shell and can accomodate up to 2 electrons; the next shell is the "L" shell which can accomodate as many as 8 electrons; the third shell is the "M" shell with up to 18 electrons. Other outer shells such as the N-shell and the O-shell, are also possible and are occupied in atoms of the heavier elements.

The distance that an electron shell is from the nucleus of an atom depends on the total energy of that shell. The outer shells have a lower energy than the inner shells because they are further from the attractive force of the nucleus and therefore, the K-shell of an atom has a more negative energy than the L-shell, the L-shell has a more negative energy than the M-shell, and so on. The electron shells of lower negative energy are filled only after the shells of higher negative energy have been filled to capacity. The number of electrons that are in an atom of a given element can be determined from the elements atomic number.

An atom is said to exist in the "ground state" when its total energy is at the minimum (relaxed state). When an atom of an element is bombarded with x-rays, electrons in

the electron shells may be excited to the energy of unfilled shells and displaced. The process of ejecting an electron from a low to a higher level is called "excitation".(8). In order to excite an atom, the bombarding x-ray must be of sufficient energy to remove an electron from its position in an interior shell. This minimum energy is sometimes called the critical energy or absorption edge. In order to efficiently excite an electron in a given atom, the excitation beam must have an energy higher than the absorption edge of that electron. The electrons in the K-shell of an atom have higher absorption edges than those in the L-shells and the M-shells. Therefore, the x-rays must be of higher energy (KeV) to excite the K-electrons of an atom than to excite the L-electrons or M-electrons. So, if an x-ray is of high enough energy to excite the K-electrons in an atom, it is also capable of exciting the electrons in the L-shell and M-shell.

C. ELECTRON TRANSITIONS.

Once an electron is removed from an interior shell of an atom, the atom is left with a "hole" in its previously filled lowest orbitals and

is no longer in the ground state. The atom will "relax" back to its ground state when an electron from some shell of lower negative energy moves into the vacant position. When the outer shell electron moves to the inner shell vacancy, it loses energy. This loss of energy is accompanied by the emission of electromagnetic radiation, the energy of which is in the range of energies classified as x-rays (0.5 to 125 KeV). (5). Figure (3) shows (a) the creation of a K-shell vacancy by an incoming electron of energy E_K sufficient to eject the K-shell electron, and (b) the transition of an L-shell electron to fill the K-shell vacancy with the corresponding emission of an x-ray of energy K.

D. X-RAY ENERGIES.

The magnitude of the energy of the x-ray emitted when an outer-shell electron fills a newly created electron vacancy depends upon the transition involved and the element being excited. The energy of the released x-ray is determined by the difference between the original energy level of the electron and its new energy, in the inner shell, after it has made the transition. X-ray energies are named after the type of transition involved. For example, "K" x-rays result from a transition of outer shell electrons to K-shell va-

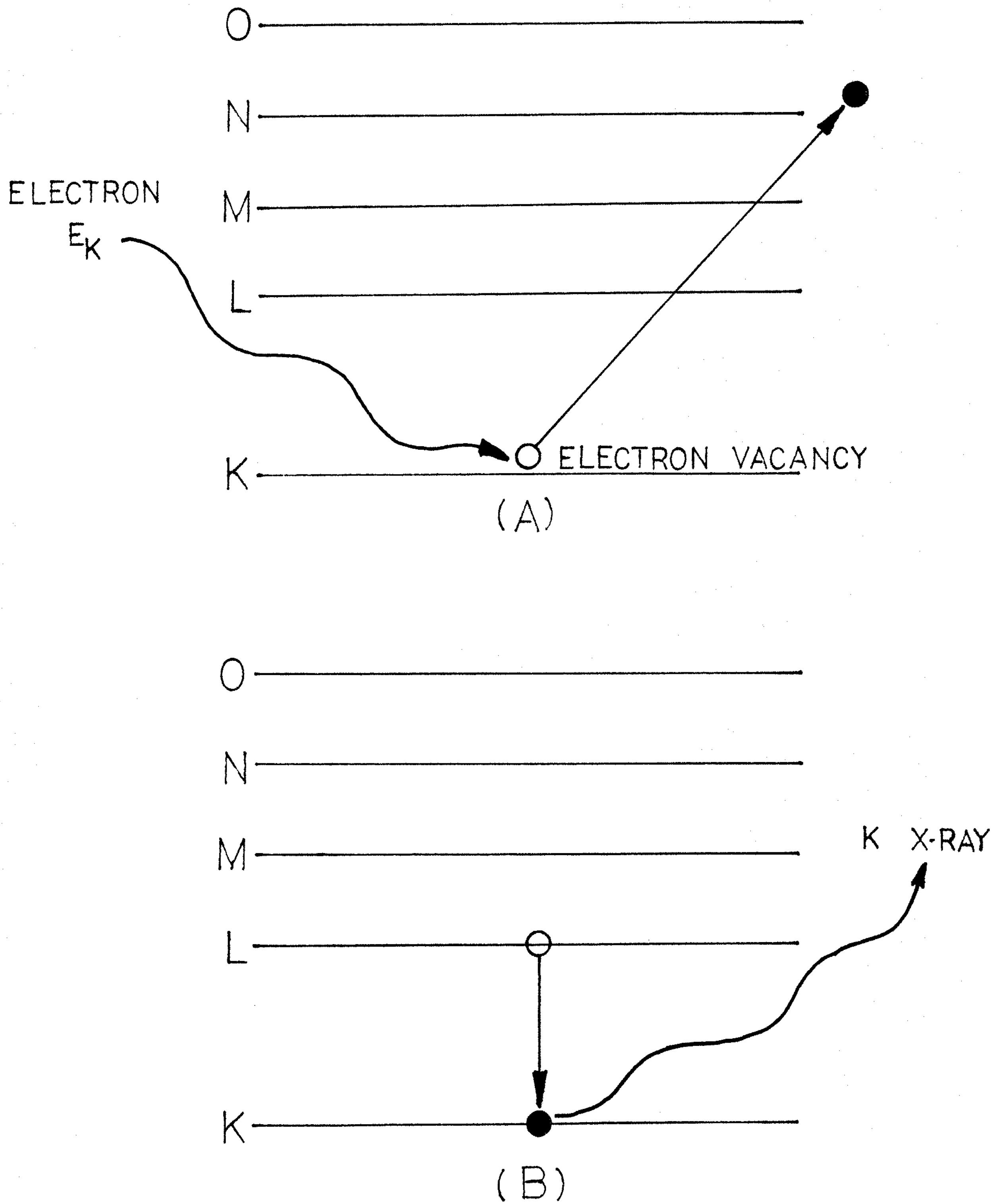


Fig. (3). K X-RAY TRANSITIONS.

cancies; "L" x-rays result from the transitions of outer shell electrons to fill L-shell electron vacancies, and so on. Figure (2) shows some of the electron transitions that result in K, L, and M x-rays. (8).

E. ENERGY SUBSHELLS.

The atomic model shown in figure (2) illustrates the four major inner electron shells K, L, M, and N and three of the transitions that can result from electron vacancies in the K, L, and M shells. The diagram does not illustrate the possible electron subshells. Subshells exist within the major shells due to slight differences in energy between the electrons in a given major shell. The L-shell has three distinct subshells; the M-shell has five; and the N-shell has seven. The classification and names of these shells are given in Table (I). Since each subshell has a different energy, the electrons in them exist at slightly different energy levels. Because of this, the x-ray energy released when the subshell electrons make the transition to an inner shell vacancy will vary slightly. These variations account for the production of the different x-rays within an energy type. For example, K x-rays are subclassified into K-alpha (KA), K-beta (KB), and K-gamma (KG) x-rays. L x-rays are broken

TABLE (I)

X-ray Notation for the Subshells of the K, L, M and N Shells.

SHELL NOTATION	NUMBER OF POSSIBLE ELECTRONS
K	2
Total K-Electrons	2
L1	2
L2	2
L3	4
Total L-Electrons	8
M1	2
M2	2
M3	4
M4	4
M5	6
Total M-Electrons	18
N1	2
N2	2
N3	4
N4	4
N5	6
N6	6
N7	8
Total N-Electrons	32

down into L-alpha (LA). L-beta (LB), L-gamma (LG), and L-lambda (LL); and so on, with the M-series x-rays. Figure (4) shows transitions from the outer shells to the inner K-shell which may result in some of the subclasses of K x-ray energies.

F. THE XRF SYSTEM.

When the atom of an element is bombarded with x-rays of sufficient energy, electrons are removed from the structure of the atom. The atom returns to its ground state through the transition of outer shell electrons into the electron vacancies. Each electron transition results in the emission of an x-ray as indicated above. Alternatively, the transition may occur without emission of radiation. In this case the x-ray energy is transferred to another electron of the same atom and this electron is ejected. This process is called the Auger process, and the ejected electron is called an Auger electron. (11, 14). The energies of these x-rays are determined by the amount of energy lost during the transition and depend upon the structure of the atom. This in turn depends upon the number of electrons within the atom and therefore, upon the atomic number of the element. All of the x-ray energies (K, L, M, etc.) released from an excited atom make up the atom's spectrum. (3).

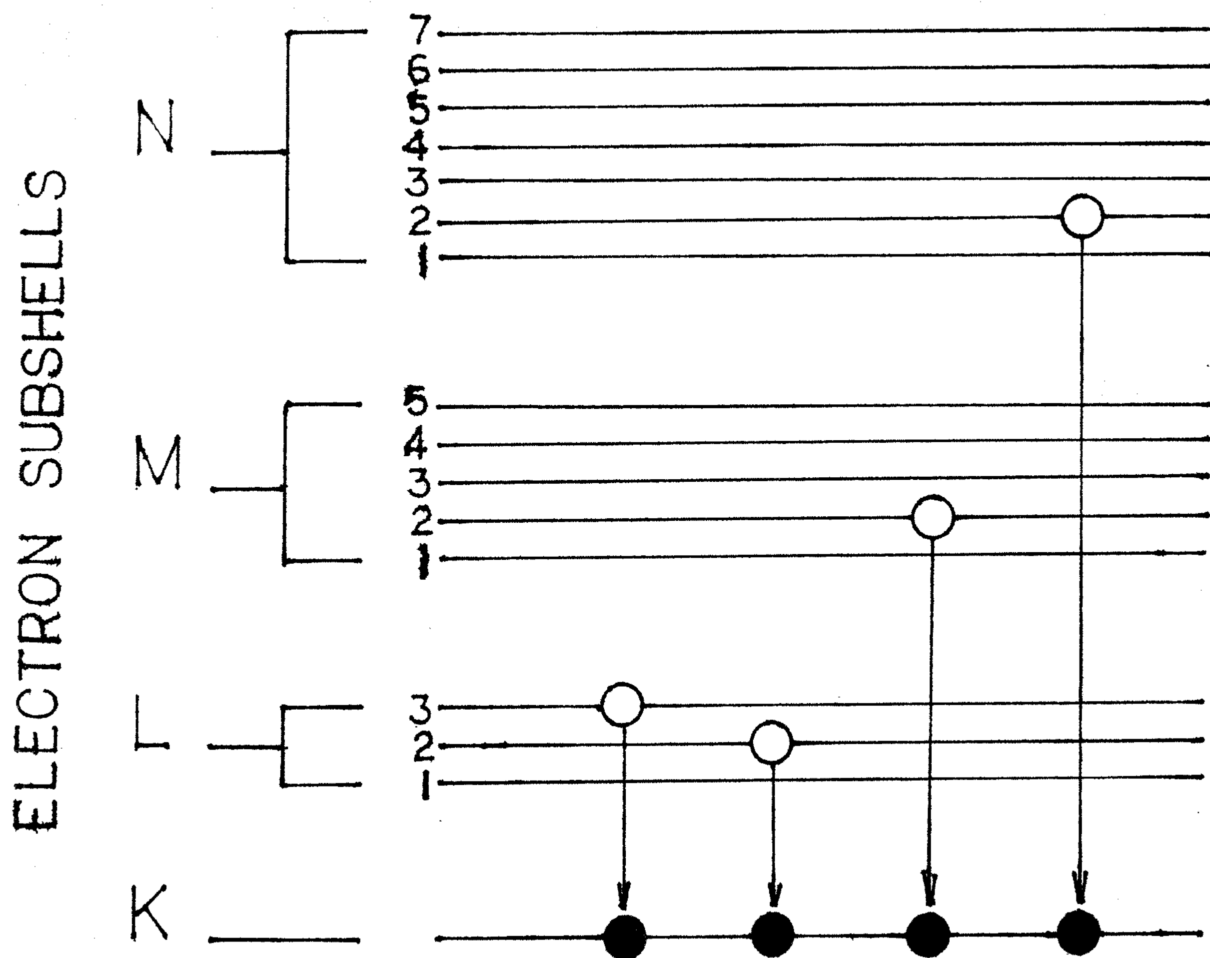


Fig.(4) ENERGY LEVEL DIAGRAM

X-rays from a sample are detected by using an x-ray detector. The x-rays emitted from an excited speciment enter through a beryllium window and strike the detectors crystal creating charge pairs in it. These charge pairs are collected by the voltege bias to form a charge pulse, which is converted into a voltage pulse that is shaped, amplified, and finally converted into a numerical value which is proportional to the energy of the x-ray that originated it. The voltages are sorted and stored as "counts" in the spectrometer and represent the x-ray energy spectrum which is displayed as a histogram of the number of x-ray counts measured in Kev. Once the spectra being analyzed are displayed on the video monitor they can be analyzed using the system's subroutines. (8).

3. METHODS OBJECTIVE

Atomic absorption spectroscopy has been the "common ground" between old and new techniques for airborne particulate analysis. Despite its advantages such as reliability, fair precision, low limits of detection, and the large number of elements which can be determined, it has a major disadvantage. It is unable to offer a modern, fast, automated (computerized), simultaneous multielement analysis. These factors compared to high manpower costs and the increasing demand for speed have outdated atomic absorption analysis.

A new promising analytical method with capability of simultaneous determination of trace elements is the inductively coupled plasma - optical emission spectroscopy (ICP-OES) system. This system is based on the observation of atomic emission spectra when samples in the form of an aerosol, thermally generated vapor, or powder are injected into an inductively coupled plasma atomization and excitation source. This method was first introduced in 1961 by Dr. Reed (9) and by 1975 was fully developed. Among the advantages of ICP-OES are the ultratrace limits (ppb) of detection, the simultaneous multielement analysis, and the elimination of interelement effects. The only disadvantage of this method compared

with the XRF method is the need for sample preparation. (9).

X-ray fluorescence is another modern approach. XRF can provide fast, accurate, and simultaneous analysis with the least effort and without the need for sample preparation. It can also execute a qualitative analysis "across the board" within minutes providing data with minimum error. Table (II) shows an intercomparison of some analytical methods. (1). But along with each method's advantages, confusion arises when detectabilities of various techniques are compared without regard for special cases of matrix interferences and the limitations imposed by the amount of sample available or by its physical and chemical form. For example, this is the case when matrix factors can affect the determination of elements adjacent in the periodic table by x-ray fluorescence. (1).

The principal scope of this thesis is to perform both XRF and AA analyses on a number of samples, correlate the results, and establish a way for reliable and reproducible quantitation.

TABLE (II). Some Analytical Techniques and Parameters.

Technique	Determined	Simultaneously	Precision (percent)	Sample preparation	Lower limit of detection
Emission spectra	Metallic elements	Yes	3-10 *1	Yes	1-10 ppm *1
X-ray spectra	Atomic #5 or above	Yes	1-5 *1	No	10-1000 ppm *1
Chemical	Most elements	No	1-5 *1	Yes	10-1000 ppm *1
Atomic absorpt.	Up to 50 elements	No	1-5 *1	Yes	0.1-100 ppm *1 in sol'n
ICP-OES	Up to 65 elements	Yes	1-5 *2	Yes	1-500 ppb *2 in sol'n

*1 Reference (1).

*2 Reference (9).

4. INSTRUMENTATION

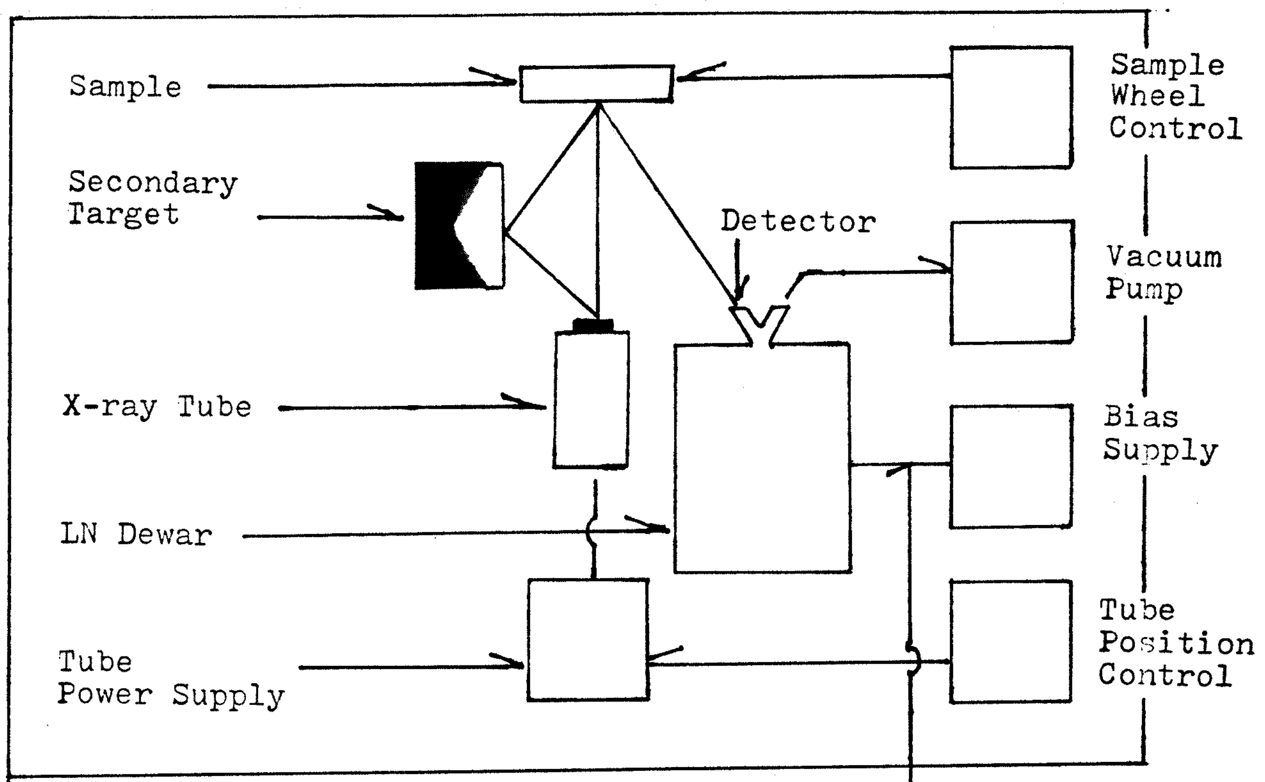
A. SYSTEM DESCRIPTION : QUANTEX-RAY

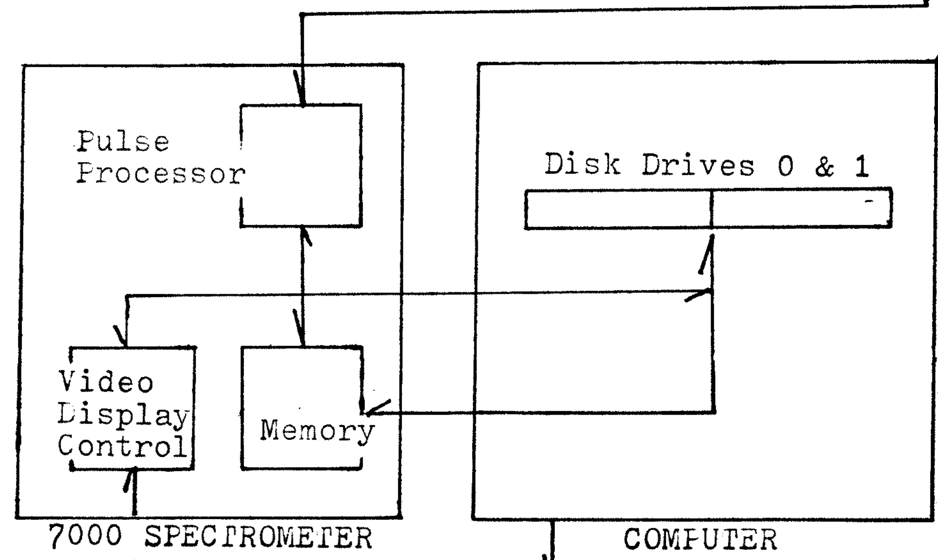
The system used for x-ray fluorescence analysis was a Energy Dispersive X-Ray Fluorescence Spectrometer, Model 7000 of Kevex Corporation. Quantex-Ray is the Kevex trademark for a computerized data acquisition and reduction system for use in x-ray spectrometry (XES). When used with a Kevex x-ray spectrometer it provides the user with sophisticated computer capability.

The main components of Quantex-Ray system are shown in fig. (5). The complete system consists of a Kevex Micro-x 7000 Analytical Spectrometer, a minicomputer, an integrated console, a dual floppy disc drive, and a printer terminal.

(a) The Spectrometer. The spectrometer is an "energy dispersive, multichannel analyzer". It provides the microelectronics circuitry that collects, processes, and stores x-ray signals coming to the detector according to their energies. The number of signals stored in the spectrometer memory, can be displayed as x-ray spectra and analyzed using the Quantex-ray system.

(b) The Minicomputer. The minicomputer provides the central





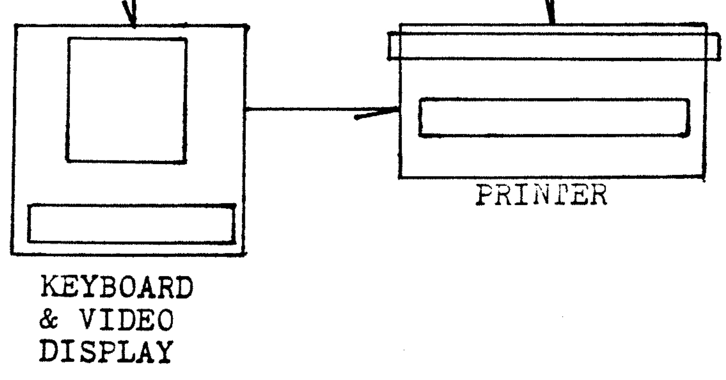


Fig. (5)

Diagram of the Quantex-Ray system.

processing for the Quantex-Ray system. It can be programmed to organize complicated tasks and perform involved calculations. The minicomputer is equipped to handle all the filing, data processing, and control tasks required by Quantex.

(c) The Console Keyboard. The integrated console/display has two functions: (1) the keyboard serves as an input terminal for the Quantex commands and the 7000 firmware interactive functions; (2) the display provides visual output of data to allow the user to inspect data and observe the results of data reduction.

(d) The Floppy Disk Drive. The dual floppy disk drive provides the Quantex-Ray system with external data and program storage. This increases the storage and computing capacity of the system. The operating system program and data files can be stored on the floppy disks and retrieved from them at any time. When certain command routines or files are needed, they can be retrieved, loaded into the internal memory and accessed. This allows for the most efficient use of the computer's memory capacity.

(e) The Printer Terminal. The printer terminal gives the Quantex-Ray sustem the capacity of providing hard copy print-

outs of analytical results, and plots of displayed spectra.

(f) The XRF System. The XRF subsystem provides the source of x-ray signals to the Quantex-Ray system. The XRF system contains a source of x-rays to excite the sample and a Kevex x-ray detector to detect the x-rays fluoresced from the sample. The fluoresced x-rays from the sample contain qualitative and quantitative information on the elements in the sample. The Quantex Ray system is used to extract this information from the x-rays.

The XRF subsystem may also be controlled from the Quantex-Ray computer. For example, the 7000 XRF subsystem can have the sample position and the excitation conditions controlled from the computer.(8).

5. PREPARATION OF ANALYSIS AND SELECTION OF CONDITIONS

A. ELEMENTS TO BE ANALYZED

The elements examined in this analysis are eight metals from the first transition series and lead. The x-ray emission lines for elements to be analyzed are shown in table (III).

ATOMIC NUMBER	ELEMENT	X-RAY EMISSION LINES (KeV) KA1	KB1	LA1	LB1
22	Ti	4.5	4.9	0.5	0.5
23	V	5.0	5.4	0.5	0.5
24	Cr	5.4	6.0	0.6	0.6
25	Mn	5.9	6.5	0.6	0.6
26	Fe	6.4	7.1	0.7	0.7
28	Ni	7.5	8.3	0.9	0.9
29	Cu	8.0	8.9	0.9	0.9
30	Zn	8.6	9.6	1.0	1.0
82	Pb			10.6	12.6

* Sc KA1 lines overlap heavily with Ca KB1 lines.

* Co KA1 lines overlap heavily with Fe KB1 lines.

* The elements Sc and Co were excluded in order to avoid overlapping problems.

B. SELECTION OF FILTER

The paper filter used in this analysis was a quartz microfiber, QM-A Whatman filter paper manufactured from pure silica fibers, acid washed and leached to achieve a purity of 99.6 % SiO_2 . It is also binder free but contains 5 % pure borosilicate glass microfibers to improve strength and durability. This paper offers high particle retention efficiencies while retaining high flow rates. It also contains low levels of heavy metals which allow critical trace metal levels to be determined with accuracy.

Other kinds of filter papers such as the Whatman glass fiber, the Whatman glass microfiber, and teflon filter were also tested. An XRF analysis performed on these filter papers showed that the Whatman quartz microfiber filter produced the lower background required for this analysis.

The samples for this analysis were high volume collected suspended air particulates.

C. SELECTION OF EXCITATION CONDITIONS.

Selection of excitation conditions in an x-ray analysis involves selecting an excitation source (target) and determining the optimum voltage (KV) and intensity (MA) settings. Selection of the excitation conditions depends on the excita-

tion efficiency for the elements being analyzed, and its effect on scatter (background) and sample counting statistics.

1. Target Selection.

The x-ray excitation energy is the energy available in each x-ray photon to lift an electron free from its subshell. This process requires a minimum or "critical" energy equal to the binding energy of the electron. The analytical efficiency for a given element is increased by exciting it with an energy as close to, but higher than, the binding (or absorption edge) energy as possible. Thus the target is chosen such that it gives x-rays above the absorption edges of the elements of interest, but not too far above.

There are three types of excitation : (a) Direct Excitation, (b) Filtered Direct Excitation, and (c) Secondary Excitation. The direct excitation is done by having the x-ray beam shine directly on the sample. It can provide a beam of higher intensity (flux) at low energies. and it is normally used for exciting lower energy lines (e.g., Si, Al). In the filtered excitation, primary beam filters can be used to modify the direct excitation beam by selectively removing part of the incoming beam energy spectrum. In general there are two types of filters used; white filters which contain no

absorption edges and are used to remove the low energy background "noise" (bremsstrahlung) from the primary beam, and edge filters which use the absorption edge of the filter material to selectively pass energies just below the edge and remove them above the edge. Finally, secondary target excitation is used to provide a nearly monochromatic source of x-rays to excite the sample. The primary beam from the x-ray excites the secondary target, and then the characteristic lines from the target are used to excite the sample. This allows the instrument to provide very low background under the peaks of interest, excite the lines of interest more efficiently, and make the parameter equations simpler.

Before deciding on a set of excitation conditions to be used, a qualitative analysis of the samples should be performed. A qualitative survey of the sample will provide information useful for selecting excitation conditions and standards by providing information as to the composition of the sample.

Considering the above and the important factors of maximum yield (highest counting rate per unit concentration of analyte) and minimum background (highest possible peak-to-background ratio), a germanium (GE) secondary target was used in

this analysis. The germanium target provides a KA-line of 9.88 KeV, and has an absorption edge capable of exciting all the elements of interest. Lead has higher Kev x-ray emission lines (10.6 KeV), but GE target was able to provide the energy needed in order to achieve high counting rate per unit concentration values. without the use of a second target.

2. Optimum KV Settings.

The most efficient excitation of the secondary target will be achieved by selecting a kilovoltage (KV) value that places the intensity maximum to an energy close to, or slightly greater than the absorption edge of the secondary target used. Since the intensity maximum of the x-ray tube's continuum output (bremsstrahlung) is located at approximately 2/3 of the energy maximum, the KV should be set to roughly 1.5 times the energy of the absorption edge of the secondary target material. Using the above rule for germanium secondary target the KV setting should be 1.5 times greater than the KeV value at about 15 KV.

3. Optimum mA Settings.

The optimum x-ray tube current (mA) should be adjusted to produce a dead time of 40 to 60 percent when analyzing the sample. A value of 0.60 mA was set after the secondary target and KV were selected. A list of all possible excitation conditions is shown in table (IV).

Table (IV). : A list of excitation conditions.

	TARGET	REFERENCE	KV	mA
1	GD(64)	3542.12	60	1.00
2	SN(50)	1213.45	40	1.00
3	AG(47)	2367.87	35	1.00
4	GE(32)	1638.35	15	0.60
5	FE(26)	0876.11	15	2.00
6	TI(22)	1199.42	20	2.00
7	CL(17)	0.00	0	0.00
8	CL(17)	0.00	0	0.00
18	CL(17)	1000.00	5	2.00
28	CL(17)	1314.00	7	2.00
38	CL(17)	0.00	0	0.00
48	CL(17)	0.00	0	0.00

D. SAMPLE AND STANDARD PREPARATION.

The samples analyzed by XRF analysis were parts of the filters, cut to a size of 1.5 by 2.0 inches, and enfolded in a mylar film to prevent any particulate loss in the vacuum chamber.

The standard used in the XRF analysis was acquired from the National Bureau of Standards. This was urban particulate matter standard reference material NBS SRM 1648 collected in filter bags. The material was screened through a fine - mesh sieve to remove extraneous materials and blended in a V-blender before analysis by NBS. This standard was collected over a period of 12 months and, therefore, is a time-integrated sample. For XRF analysis the standard was placed in a plastic container in the XRF chamber, so that the x-rays were able to directly strike the particulates through a mylar film. Information regarding the certified concentration values of the standard and the optimum voltage values for analysis is listed in table (V).

Table (V). Concentration and Voltage Values of NBS.

ELEMENT	KeV	CONC. WT. %
Ti	4.26-4.74	0.4000
V	4.80-5.10	0.0140
Cr	5.18-5.66	0.0430
Mn	5.70-6.08	0.0860
Fe	6.14-6.64	3.9100
Ni	7.36-7.76	0.0082
Cu	7.80-8.30	0.0609
Zn	8.40-8.88	0.4760
Pb	10.44-10.82	0.6550

6. XRF DATA ACQUISITION.

A. SAMPLE ACQUISITION.

Once the excitation conditions are established, (section 5), the analysis can start by setting :

(a) Target : secondary GE target.

(b) KV setting : 15 KV.

(c) mA setting : 2.0 mA.

In the following steps, the process of acquiring an x-ray spectrum is outlined.

ACQUISITION STEPS	ENTRY	SYSTEM RESPONSE
A. The excitation conditions are entered into the system.	SETXC	TARGET # ?
B. The samples are placed in the speciment holder.		
C. The eV/CH is set up. Since the lines of interest are between 4.5 and 10.6 KeV the spectrometer is set at 20 eV.	SETEV ENTER 20 ENTER	 EV/CH ?
D. All the data previously stored in memory group one are cleared.	CLR ENTER	

ACQUISITION STEPS	ENTRY	SYSTEM RESPONCE
E. The time of acquisition is preset at 200 seconds.	PRE ENTER	
		PRESET TIME :
	200 ENTER	
The system is now ready to acquire.		
F. Acquisition of the spectrum in memory group one is following.	ACQ ENTER	

It is important to observe the green dead time indicator while acquiring a spectrum. This indicator must be at about 40 to 60 % up the side of the spectrum.

G. When the preset time has run out the acquisition will stop. It is desirable to have at least 7000 to 8000 counts in the highest channel of the peak.

H. Once the spectrum has been acquired it can be stored on disk for further analysis, comparison, reference, etc.

ACQUISITION STEPS	ENTRY	SYSTEM RESPONSE
I. The command REA is typed so that the	REA	
spectrum displayed will be read into	ENTER	*
the data file. When the asterisk (*)	SAV	
reappears, the command SAV, is typed.	ENTER	ENTER UNIT
Then the disk on which is desired	1	
to save the spectrum is entered.	ENTER	COMMENTS
General comments such as target, eV/CH,	TARGET	
etc., are entered in order to describe	eV/CH, mA	
the spectrum.	ENTER	SPECTRUM
Finally the spectrum's ID is entered.		ID

It is useful to set up the element's list (elements of analytical interest) after each acquisition of a spectrum.

The samples analyzed by XRF were collected in the New Jersey area. The spectra of the analyzed samples are shown in figures 6 to 34, along with information regarding the location of sampling, the date of collection, and the sampling volume.

Figure (6) shows peaks assigned to the elements of interest.

QUANTEX-RAY GRAPHICS

LOCATION : BAYONNE

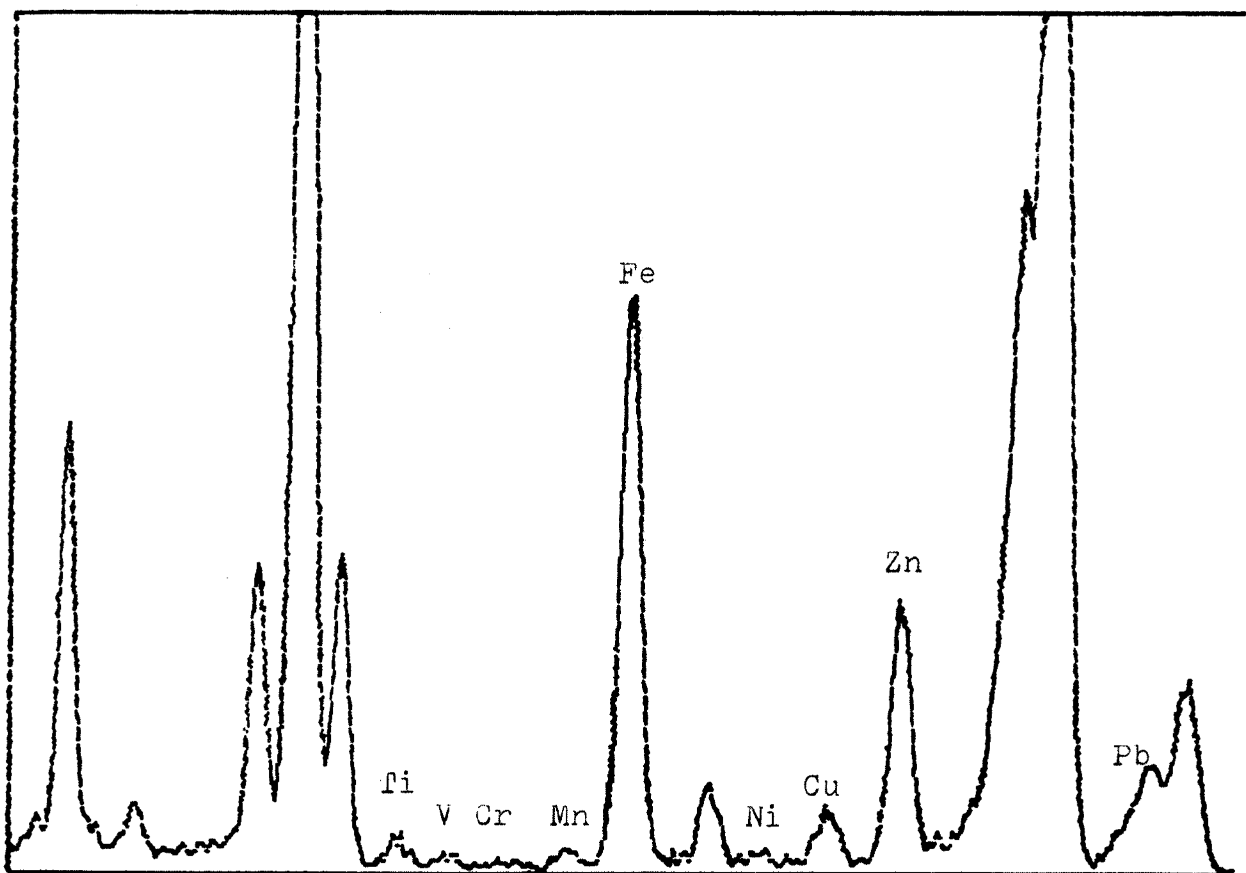
DATE : 4-29-82

VOLUME : 1830 m^3

A-002.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (6).

QUANTEX-RAY GRAPHICS

LOCATION : CARTERET

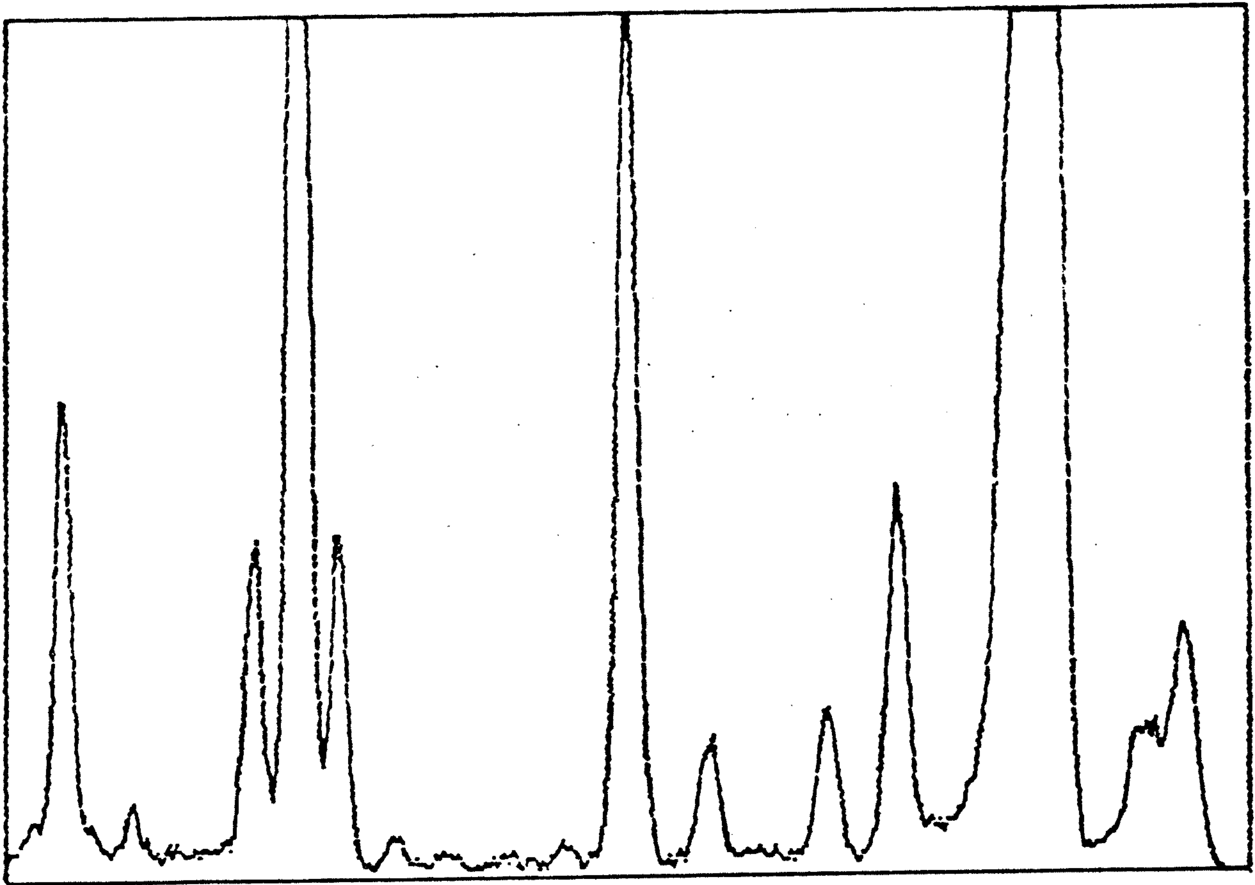
DATE : 4-29-82

VOLUME : 1789 m^3

A-005.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (7).

QUANTEX-RAY GRAPHICS

LOCATION : TOMS RIVER

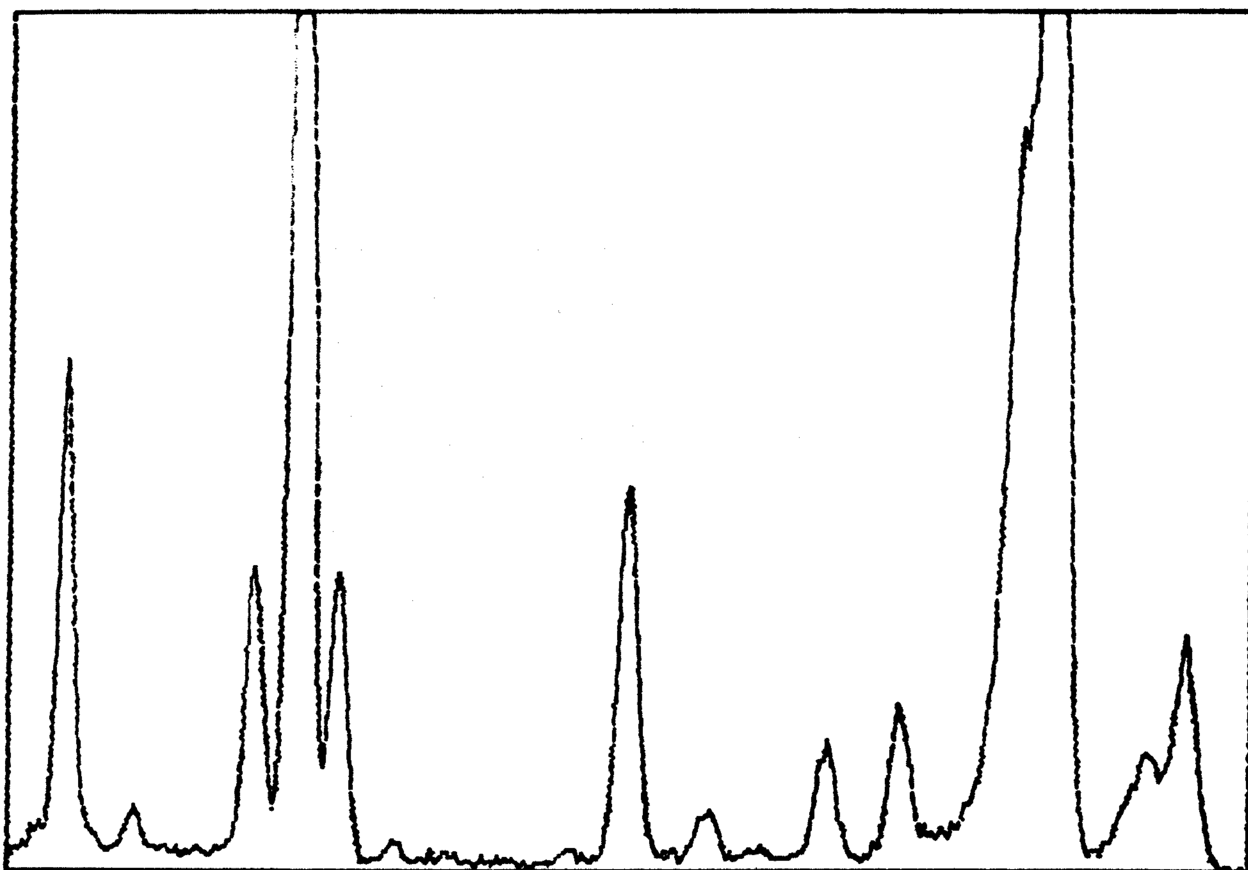
DATE : 4-29-82

VOLUME : 1828 m^3

A-040.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (8).

QUANTEX-RAY GRAPHICS

LOCATION : NEWARK

DATE : 4-29-82

VOLUME : 1875 m^3

A-044.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q

< 1.28KEV XES 11.52KEV>

Figure (9).

QUANTEX-RAY GRAPHICS

LOCATION : CAMDEN

DATE : 4-29-82

VOLUME : 1771 m^3

A-046.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q

< 1.28KEV XES 11.52KEV>

Figure (10).

QUANTEX-RAY GRAPHICS

LOCATION : FAIRLOWN

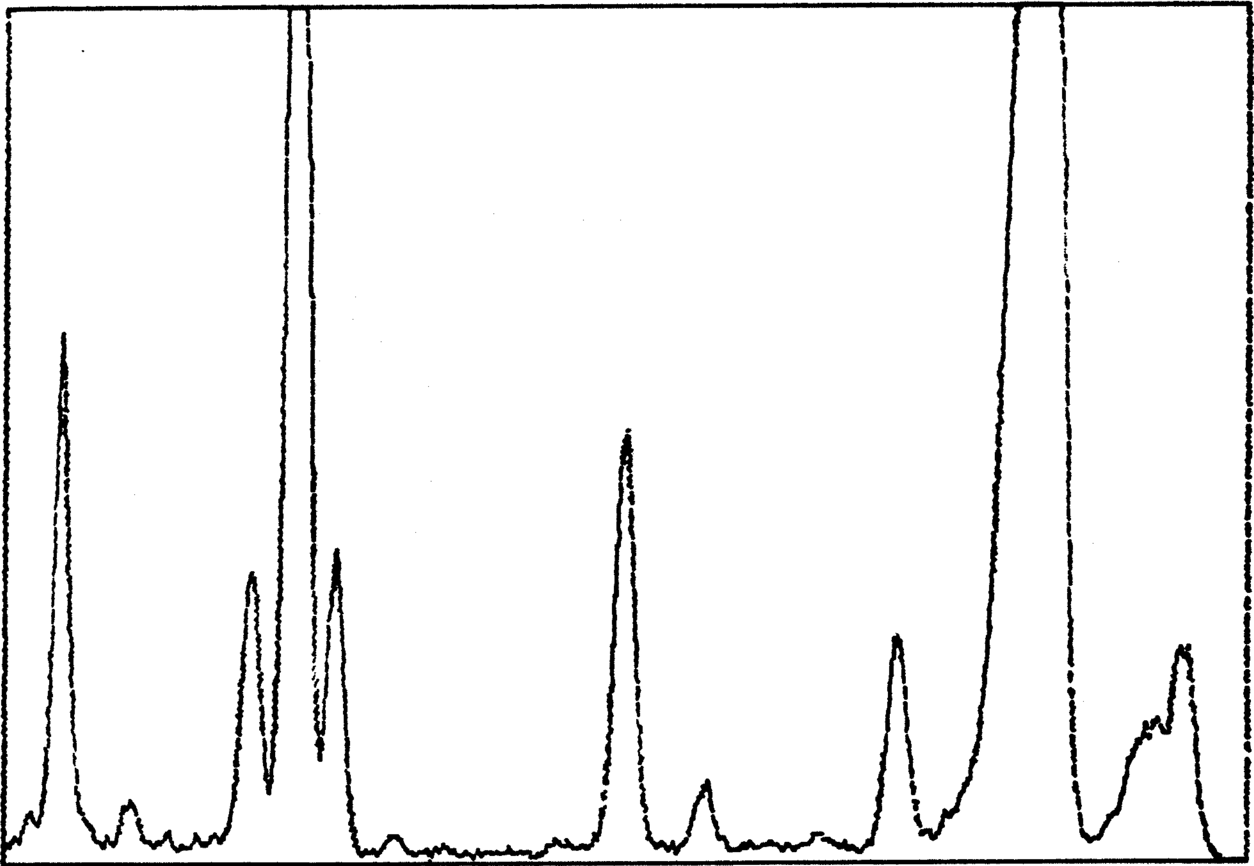
DATE : 4-29-82

VOLUME : 1940 m^3

A-S8.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (11).

QUANTEX-RAY GRAPHICS

LOCATION : CHEESEQUAKE

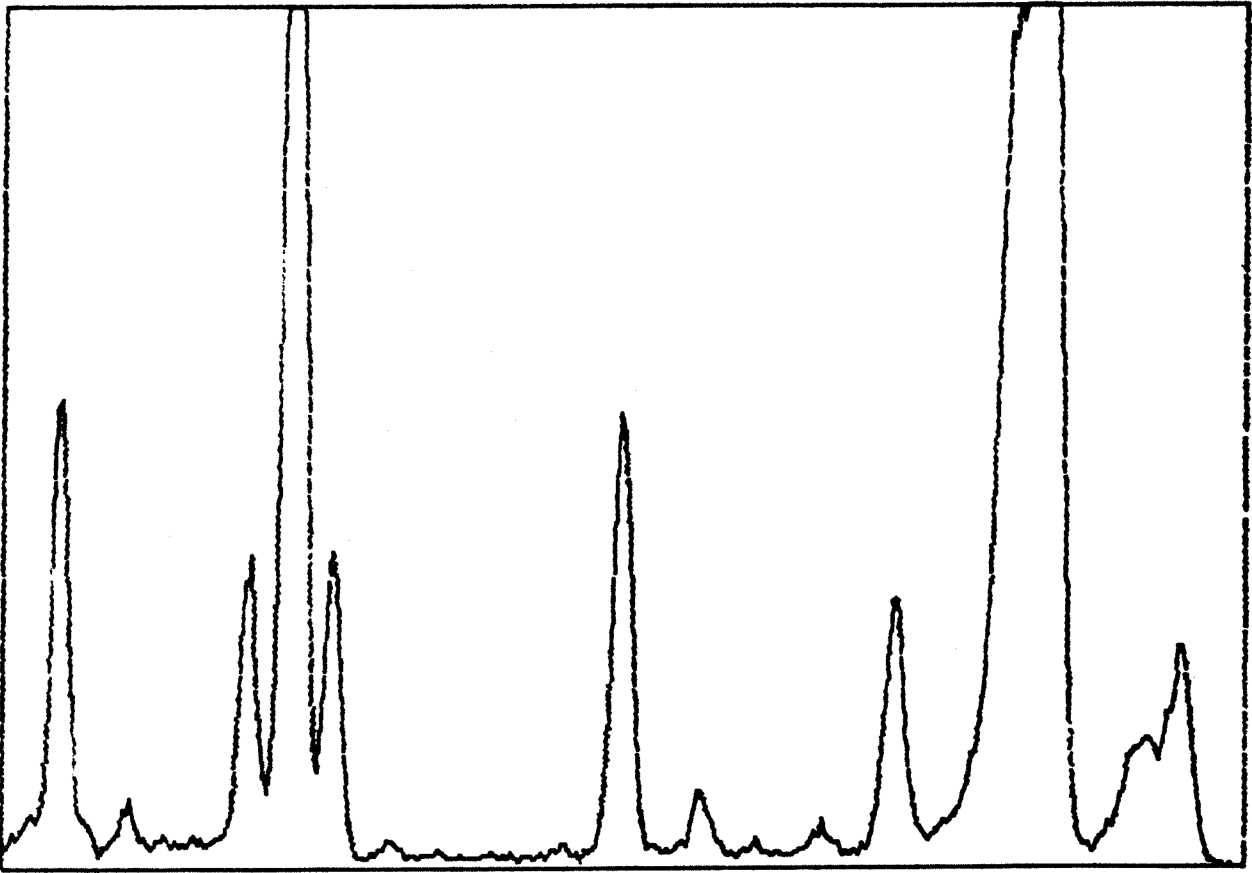
DATE : 4-29-82

VOLUME : 1868 m^3

A-S9.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (12).

QUANTEX-RAY GRAPHICS

LOCATION : METUCHEN

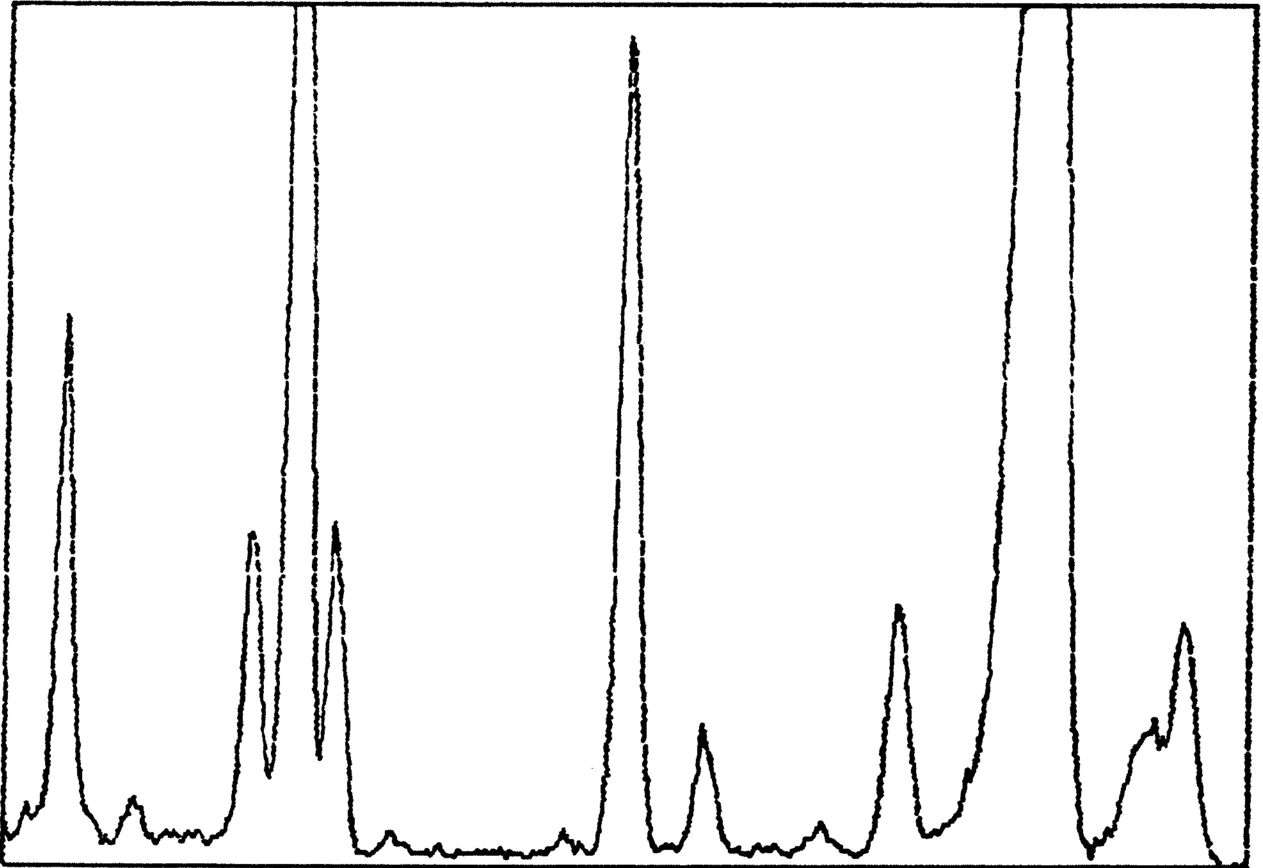
DATE : 4-29-82

VOLUME : 1864 m^3

A-S11.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (13).

QUANTEX-RAY GRAPHICS

LOCATION : PHILLIPSBURG

DATE : 4-29-82

VOLUME : 1921 m^3

A-S12.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q

< 1.28KEV XES 11.52KEV>

Figure (14).

QUANTEX-RAY GRAPHICS

LOCATION : KEAN COLLEGE

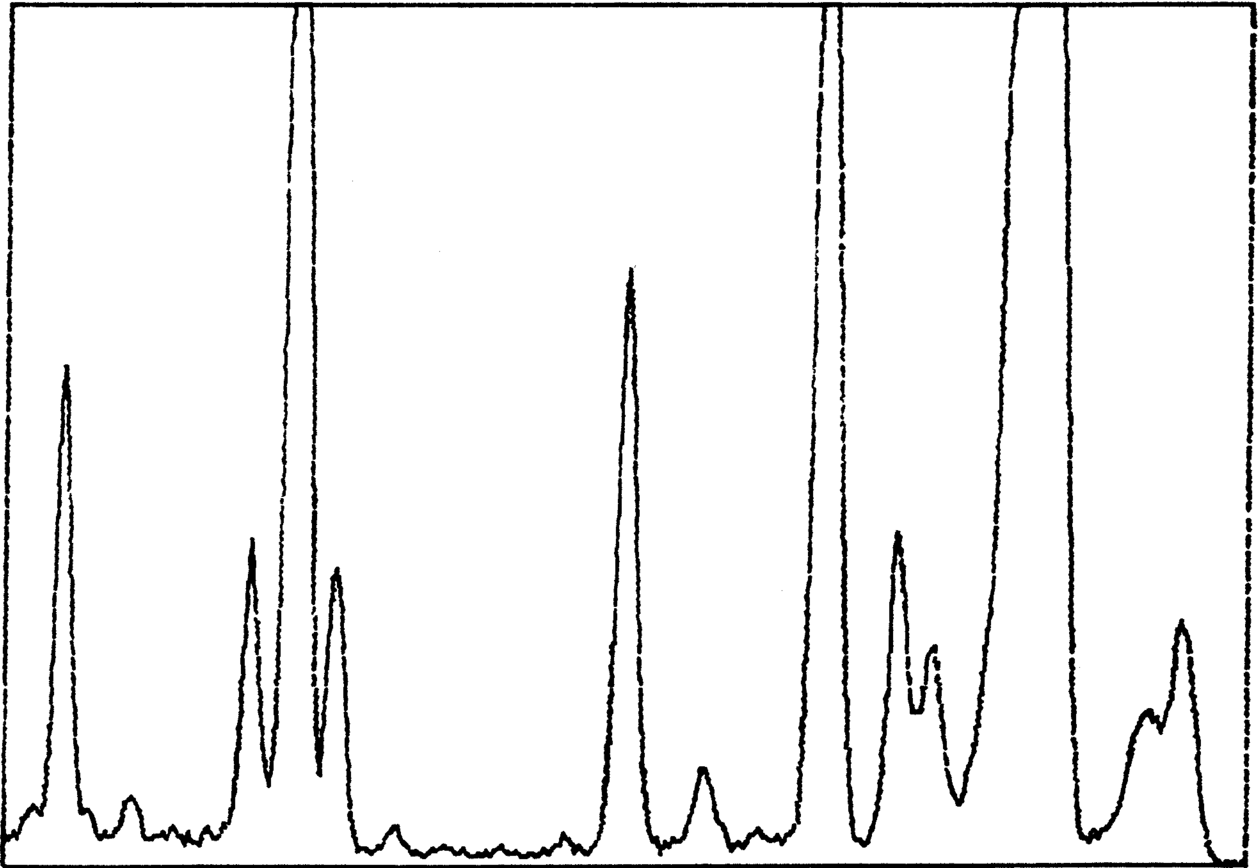
DATE : 4-29-82

VOLUME : 1821 m^3

A-S33.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (15).

QUANTEX-RAY GRAPHICS

LOCATION : TRENTON

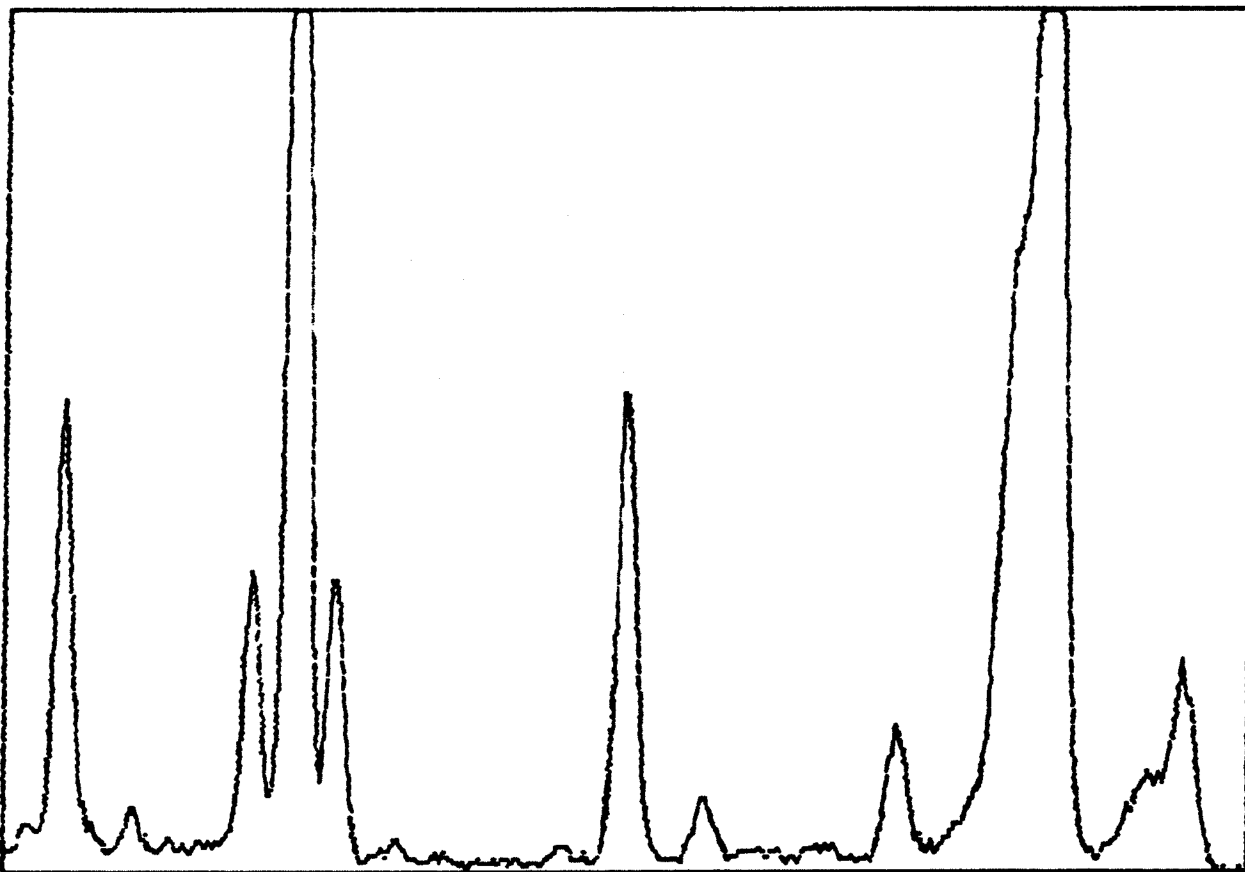
DATE : 4-29-82

VOLUME : 1848 m^3

A-S45.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (16).

QUANTEX-RAY GRAPHICS

LOCATION : HACKETTSTOWN

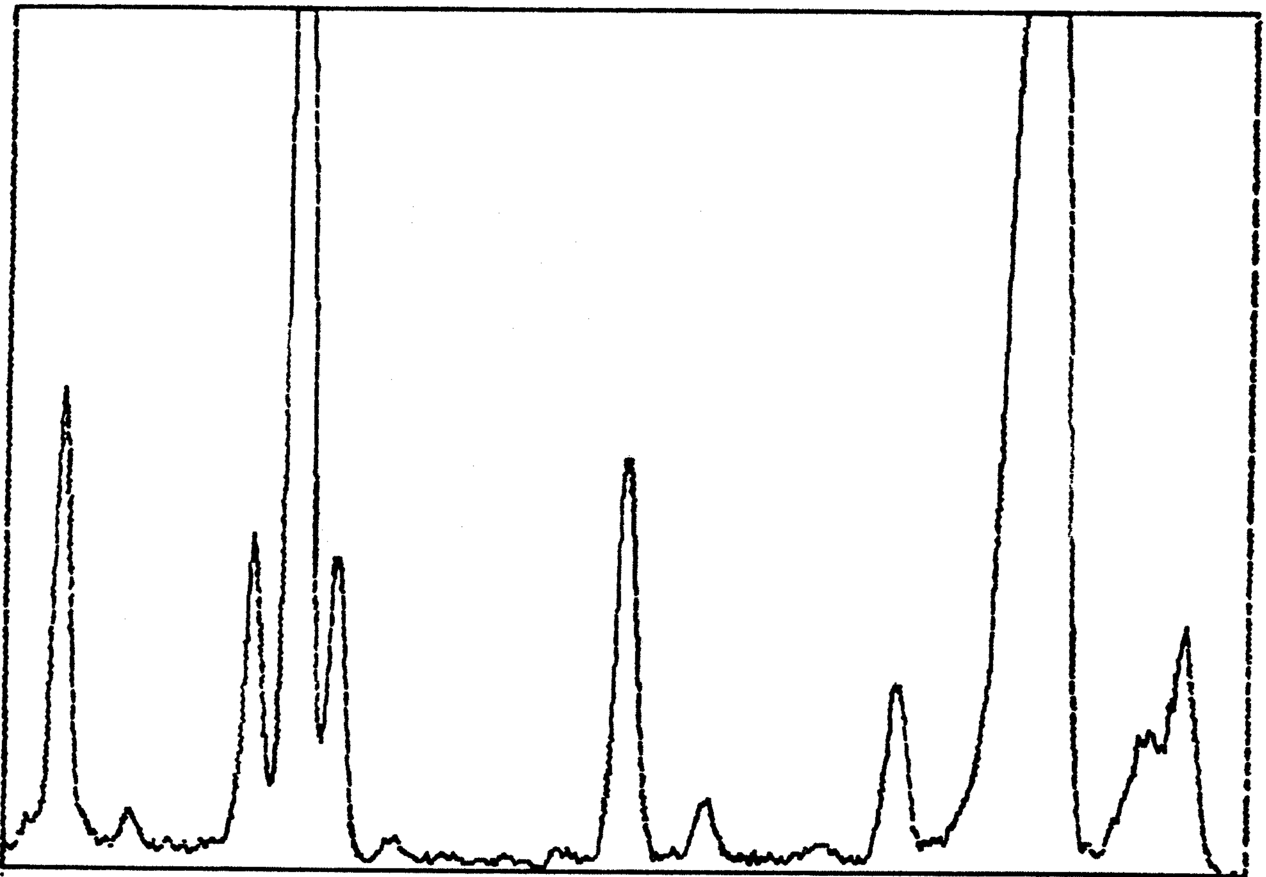
DATE : 4-29-82

VOLUME : 1842 m^3

A-549.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (17).

QUANTEX-RAY GRAPHICS

LOCATION : FRENCHTOWN

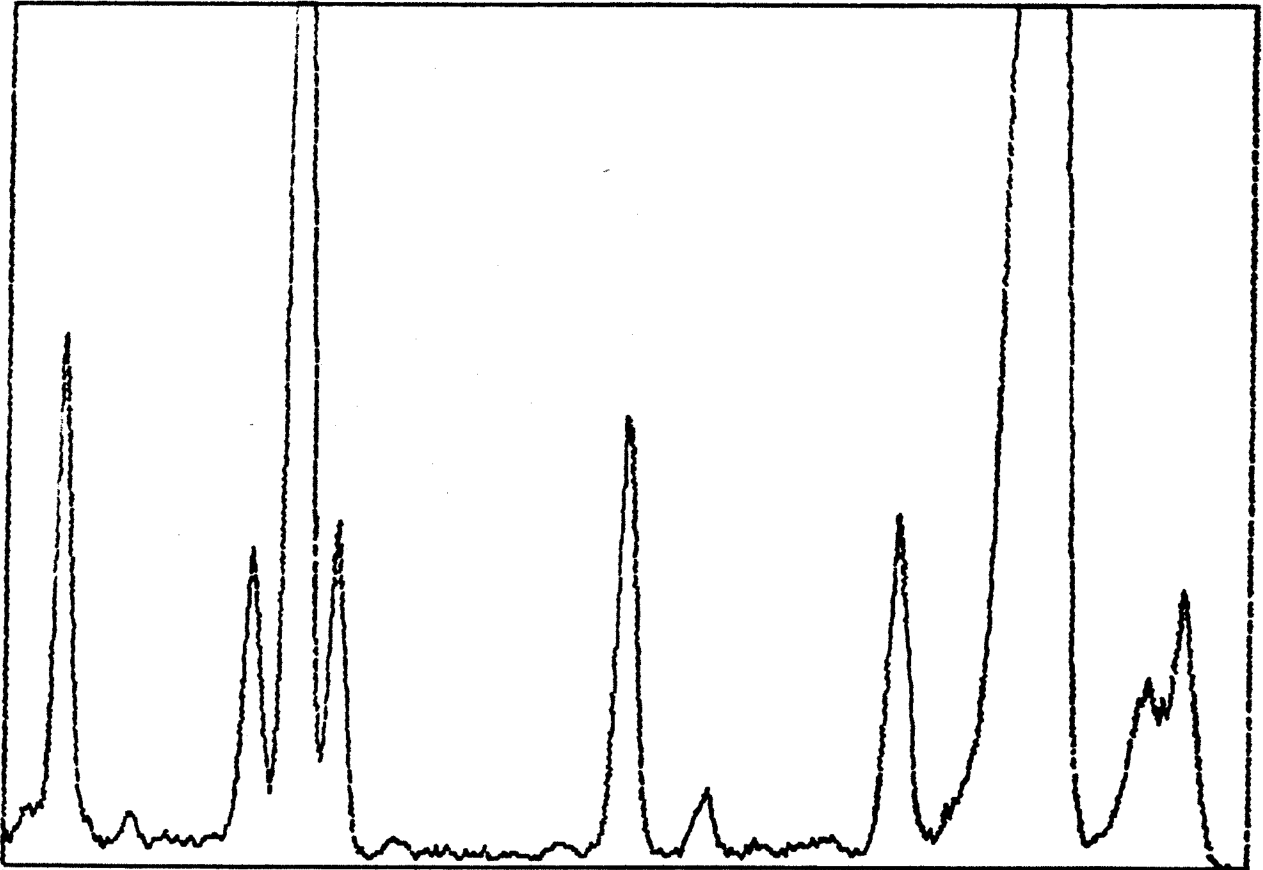
DATE : 4-29-82

VOLUME : 1857 m^3

A-S59.2

FR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (18).

QUANTEX-RAY GRAPHICS

LOCATION : PERTH AMBOY

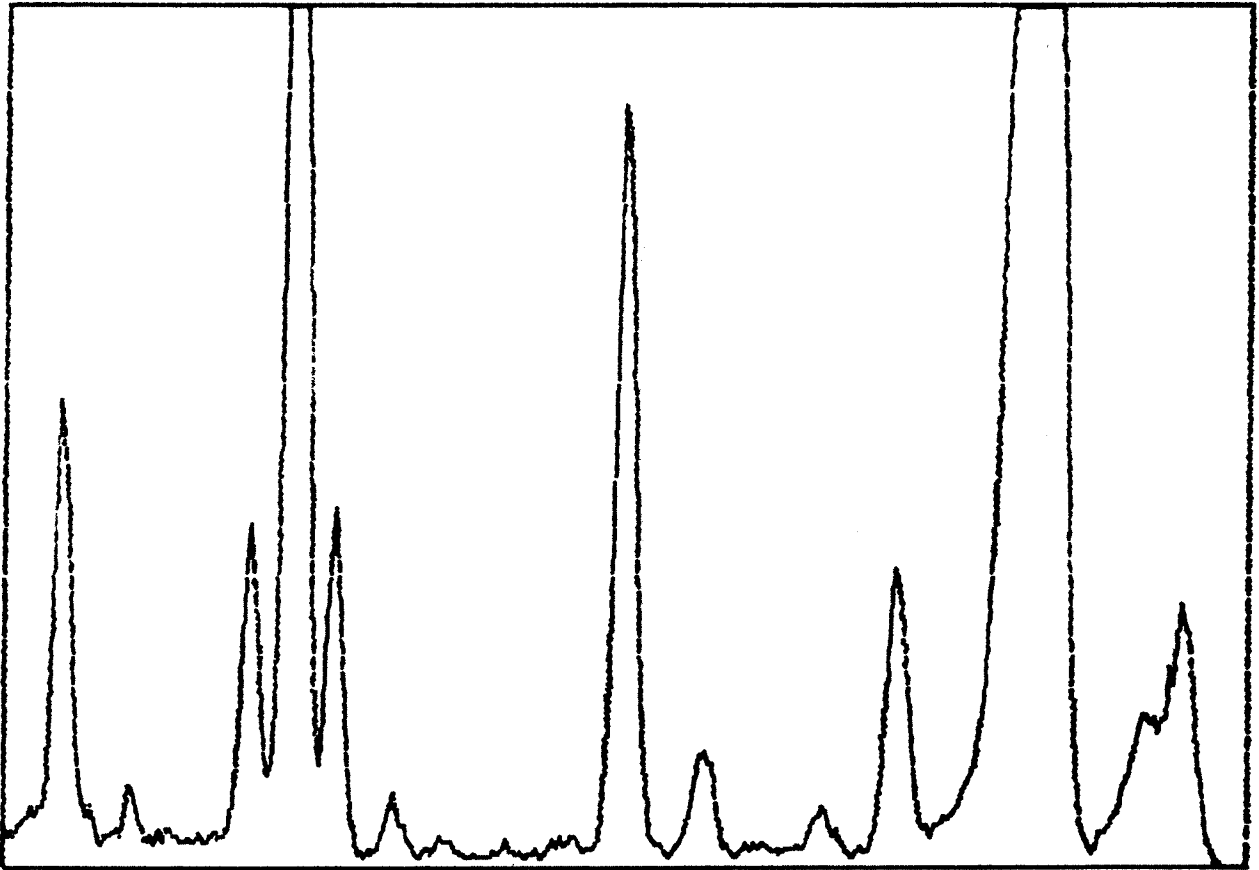
DATE : 4-29-82

VOLUME : 1858 m^3

A-S68.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (19).

QUANTEX-RAY GRAPHICS

LOCATION : JERSEY CITY

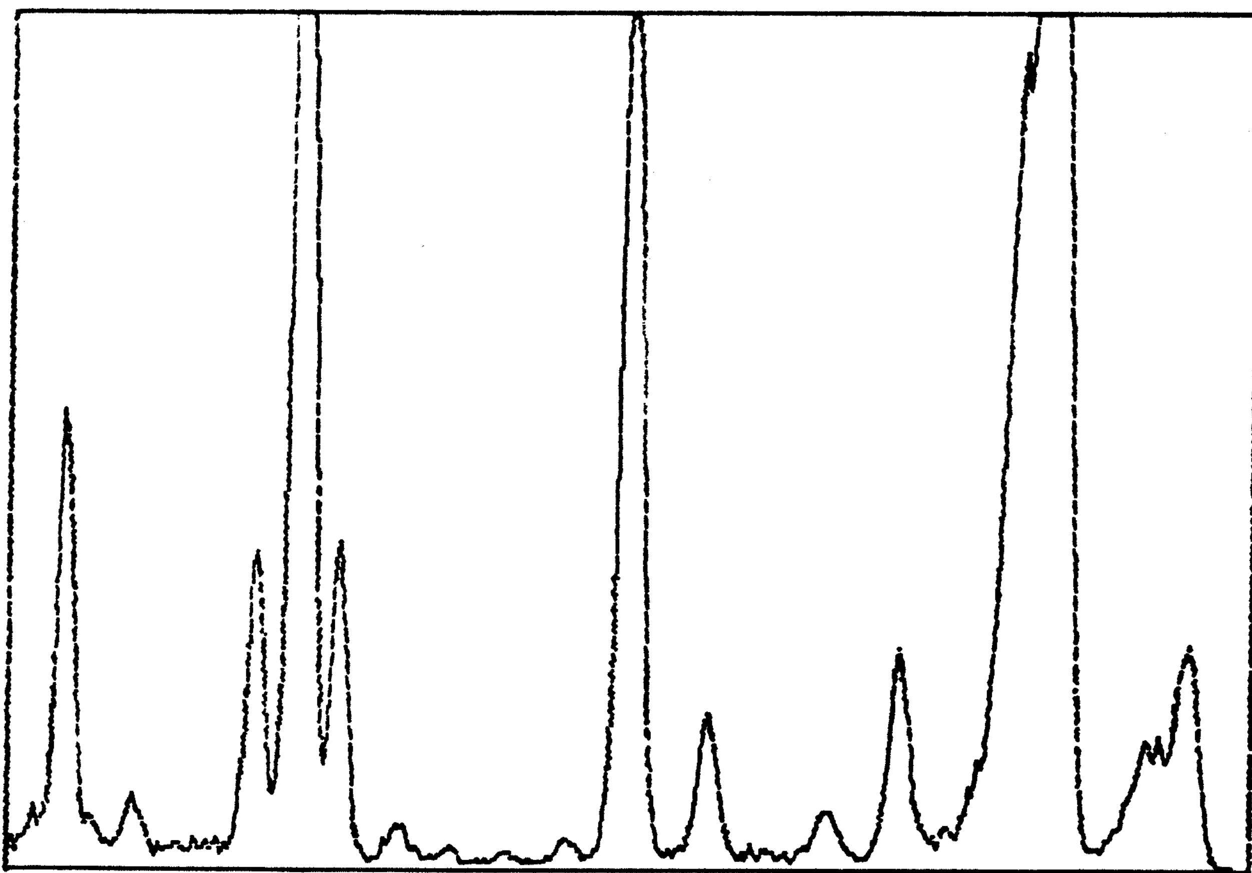
DATE : 4-29-82

VOLUME : 1882 m^3

B-015.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:10 AQ=20KEV 10



< 1.28KEV XES 11.52KEV>

Figure (20).

QUANTEX-RAY GRAPHICS

LOCATION : PILESGROVE

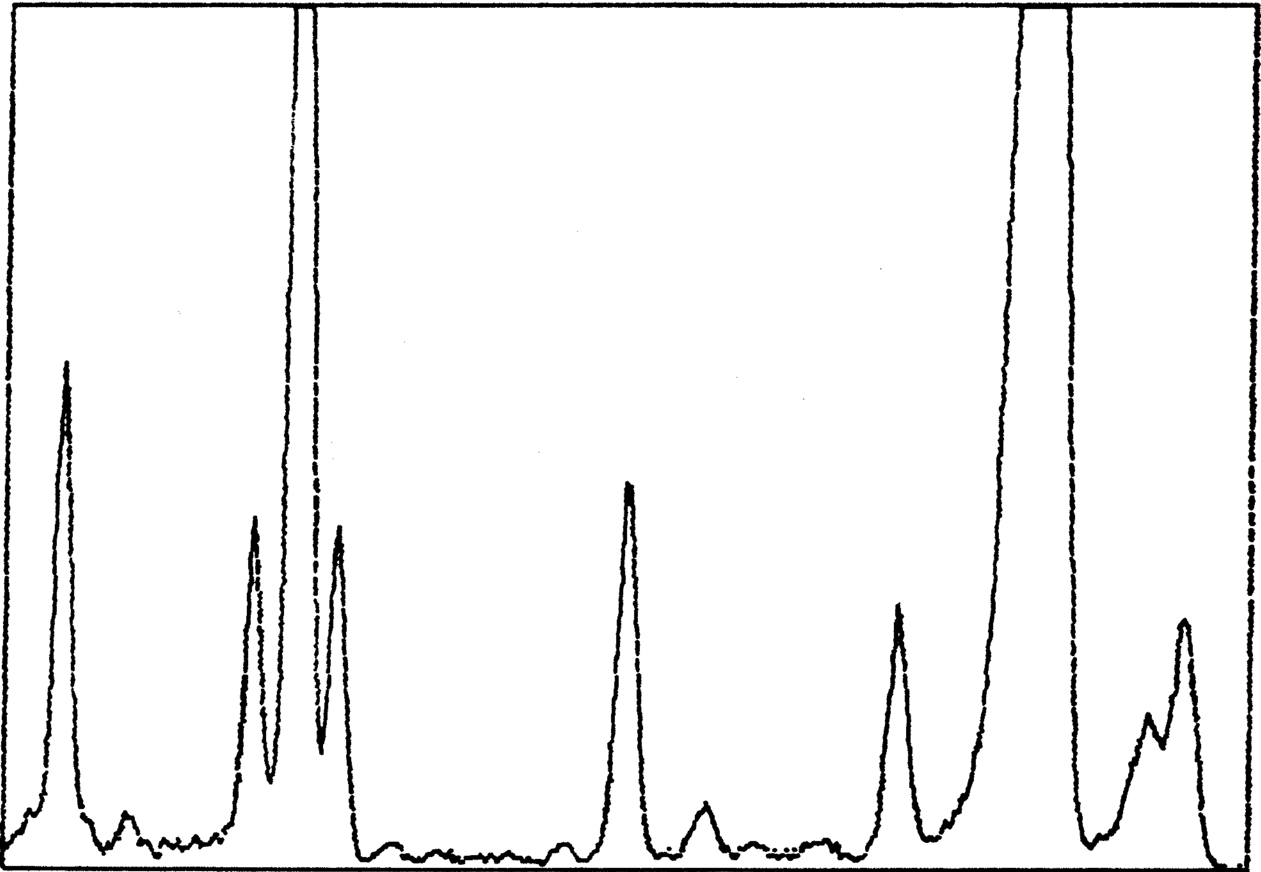
DATE : 4-29-82

VOLUME : 1859 m^3

B-S40.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (21).

QUANTEX-RAY GRAPHICS

LOCATION : HOBOKEN

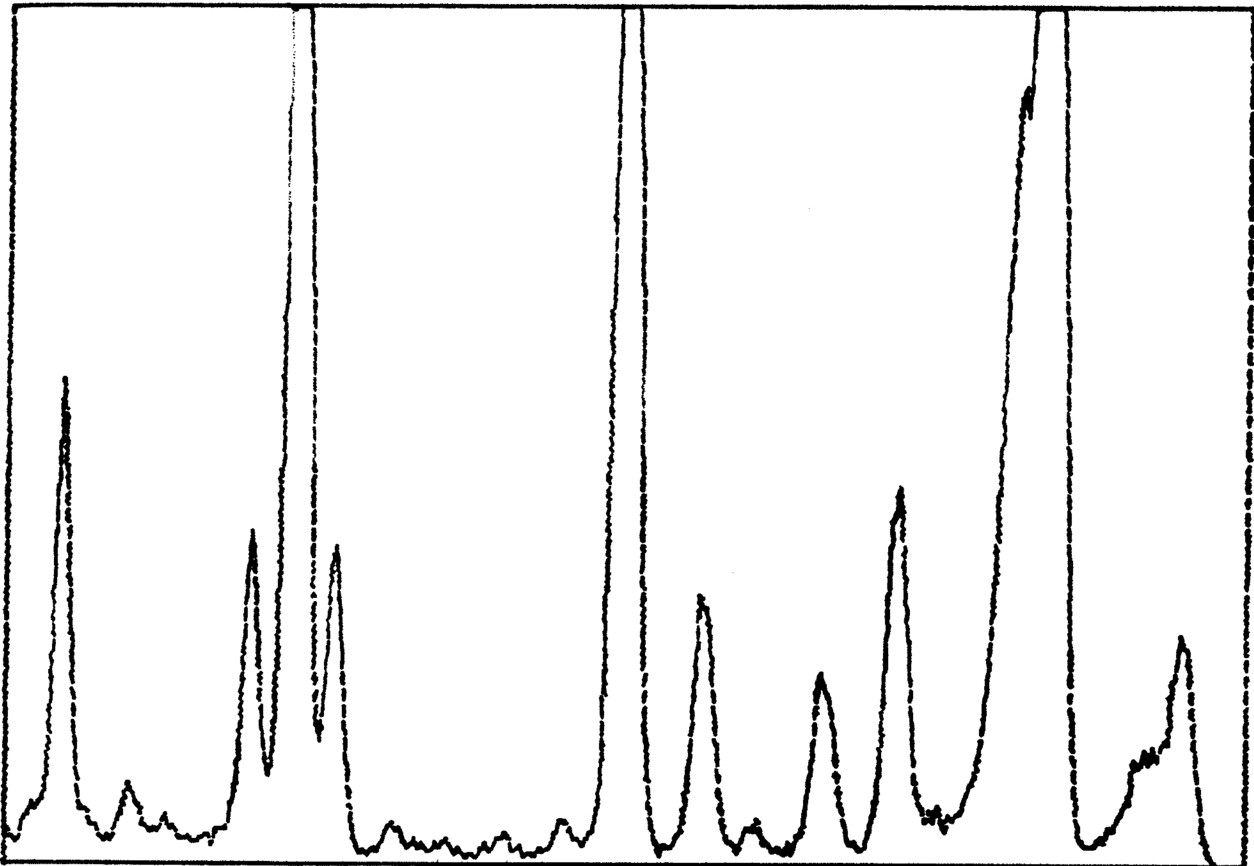
DATE : 4-29-82

VOLUME : 1832 m^3

B-S43.2

FR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (22).

QUANTEX-RAY GRAPHICS

LOCATION : JERSEY CITY

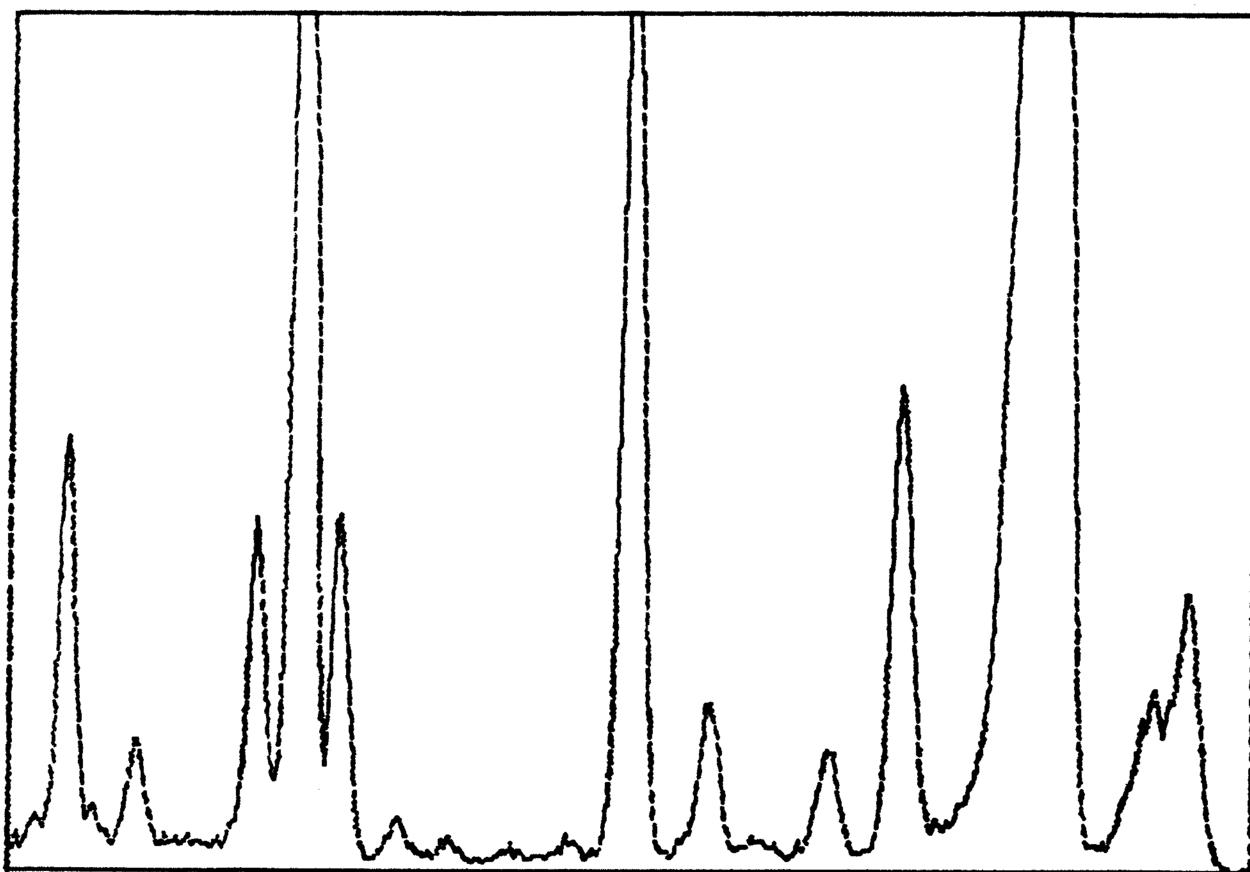
DATE : 3-24-82

VOLUME : 1942 m^3

C-015.2

FR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (23).

QUANTEX-RAY GRAPHICS

LOCATION : HOBOKEN

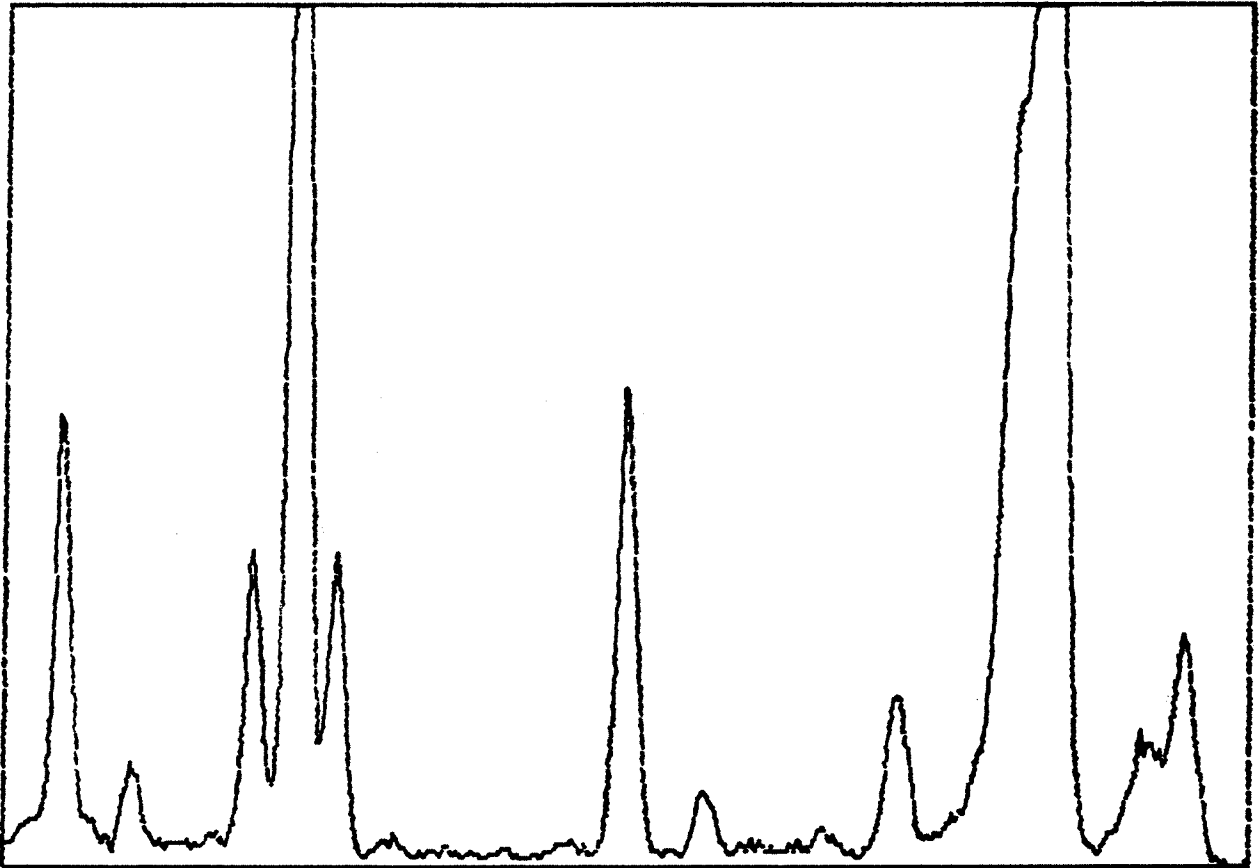
DATE : 3-12-82

VOLUME : 1812 m^3

C-S43.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (24).

QUANTEX-RAY GRAPHICS

LOCATION : ATLANTIC CITY

DATE : 3-18-82

VOLUME : 1829 m^3

C-S46.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q

< 1.28KEV XES 11.52KEV>

Figure (25).

QUANTEX-RAY GRAPHICS

LOCATION : PERTH AMBOY

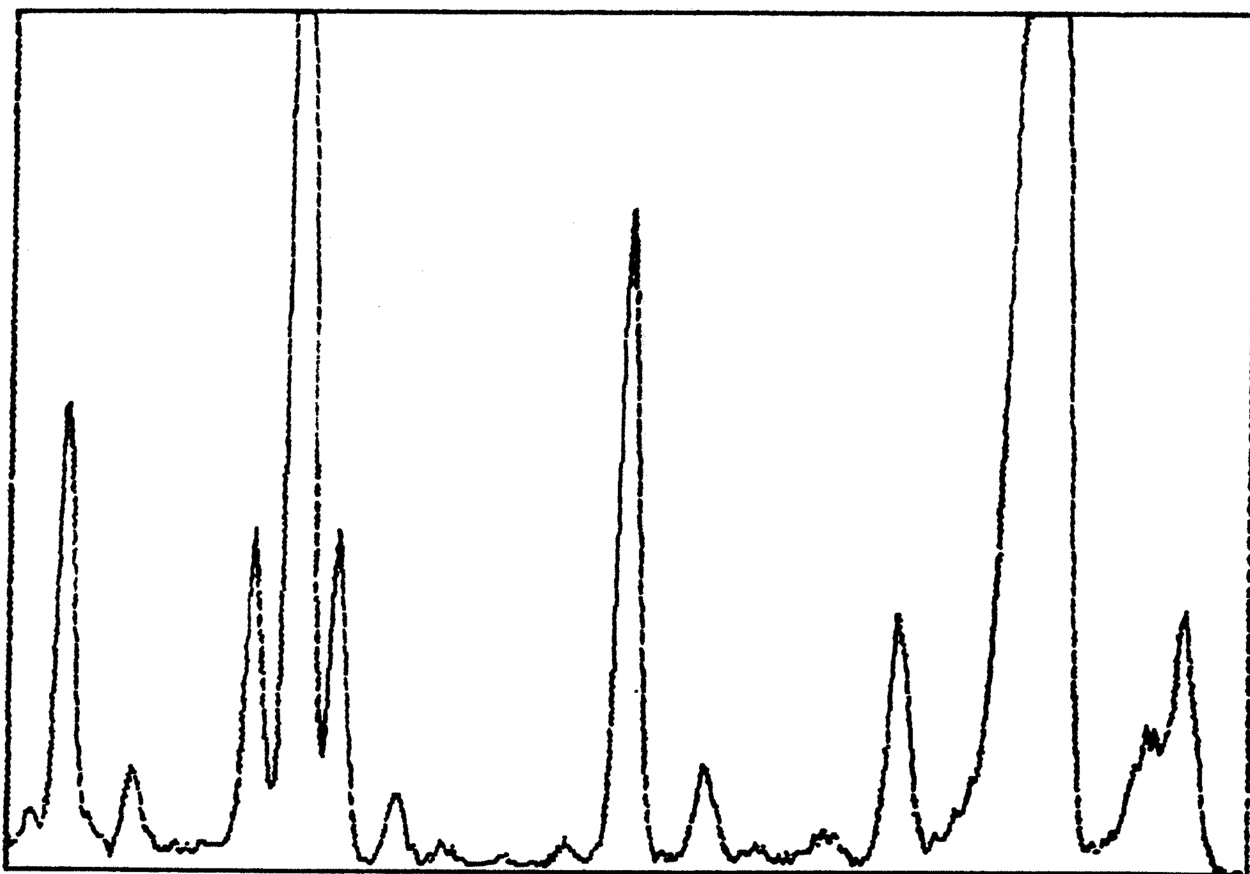
DATE : 3-12-82

VOLUME : 1740 m^3

C-S68.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (26).

QUANTEX-RAY GRAPHICS

LOCATION : JERSEY CITY

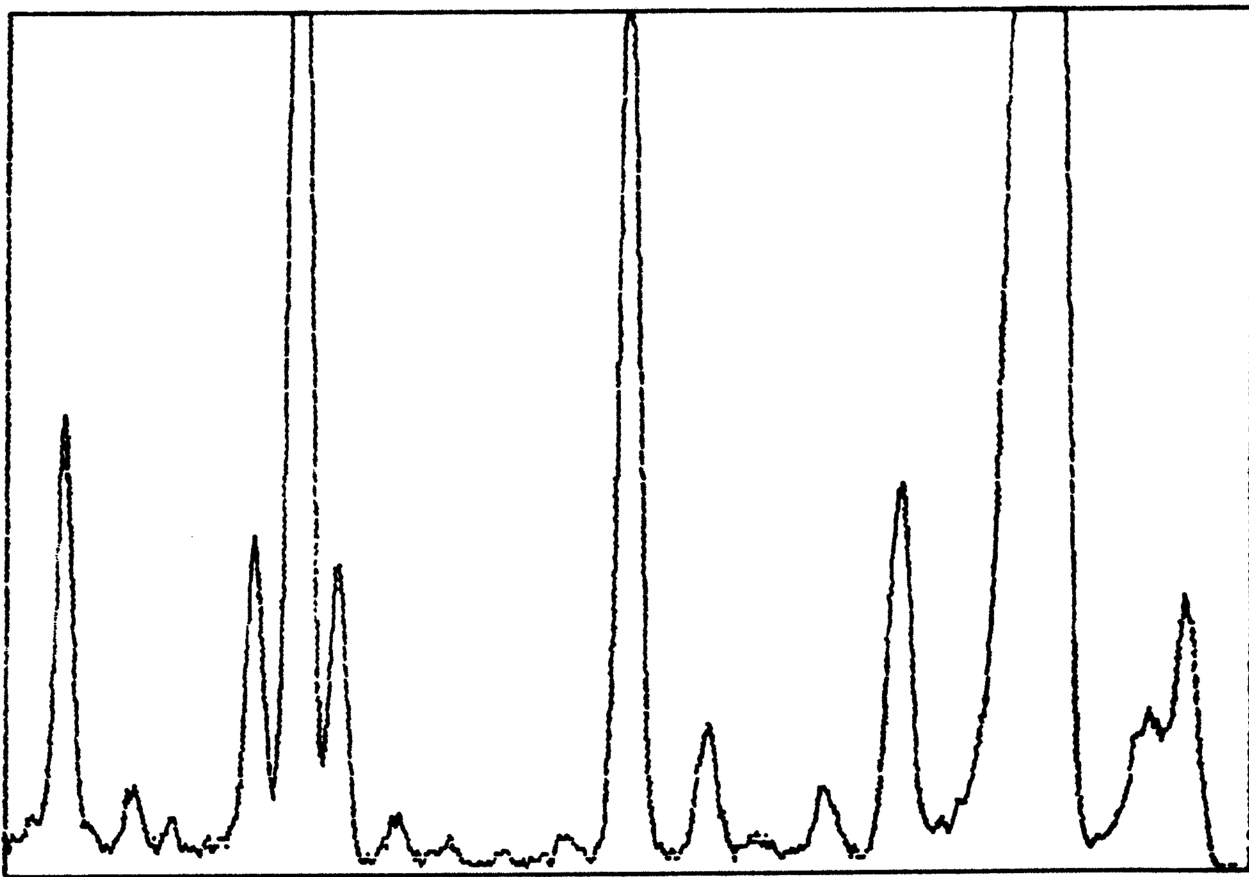
DATE : 3-30-82

VOLUME : 1993 m^3

D-015.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (27).

QUANTEX-RAY GRAPHICS

LOCATION : TOMS RIVER

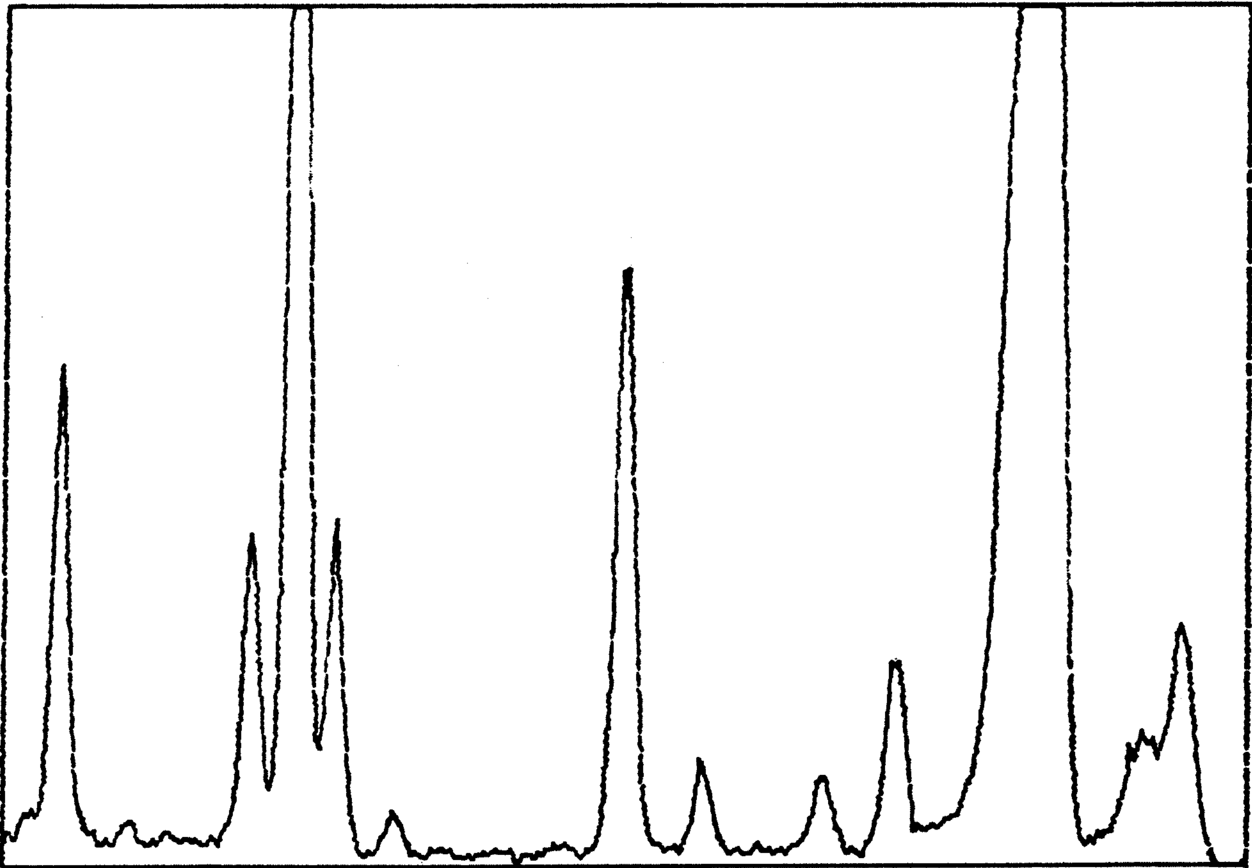
DATE : 4-5-82

VOLUME : 1880 m^3

D-040.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (28).

QUANTEX-RAY GRAPHICS

LOCATION : HOBOKEN

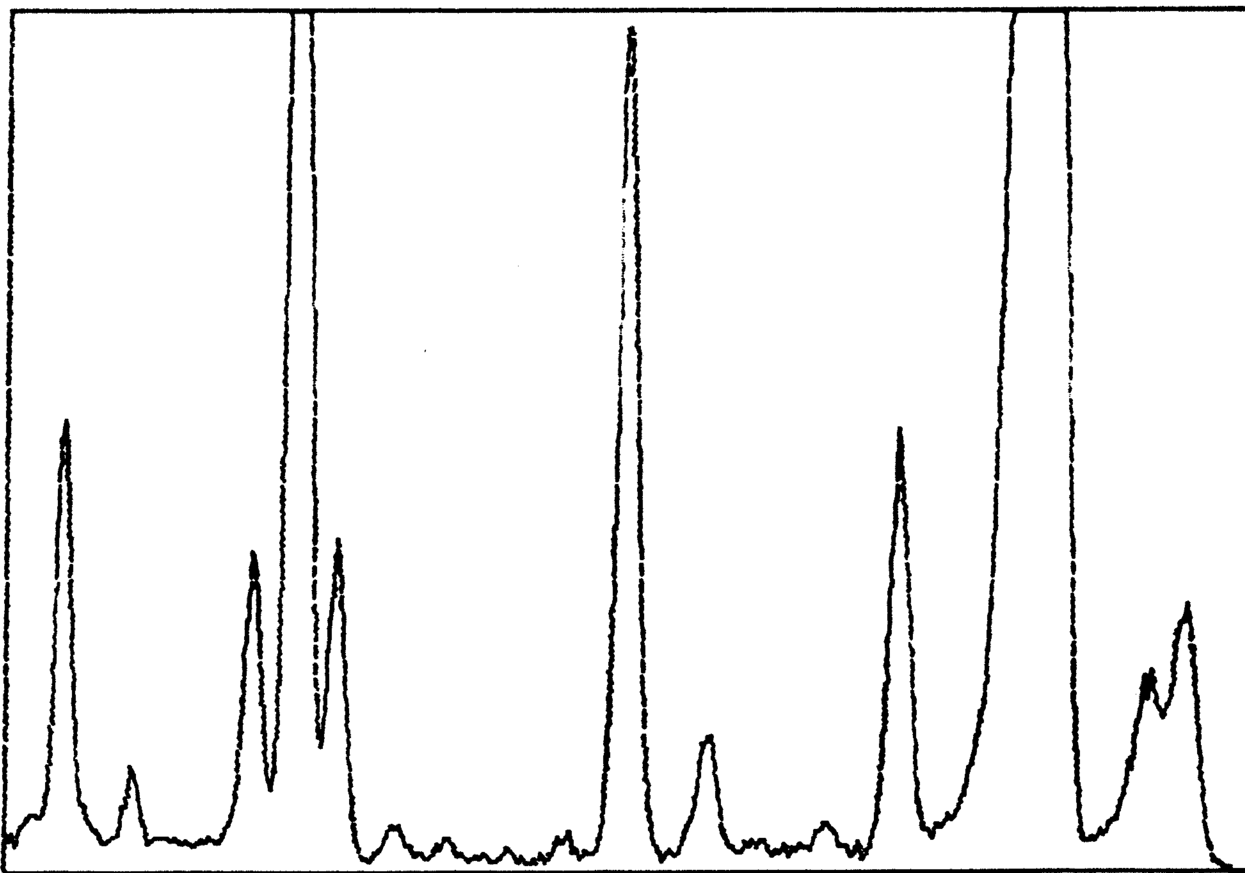
DATE : 3-30-82

VOLUME : 1841 m^3

D-S43.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (29).

QUANTEX-RAY GRAPHICS

LOCATION : ATLANTIC CITY

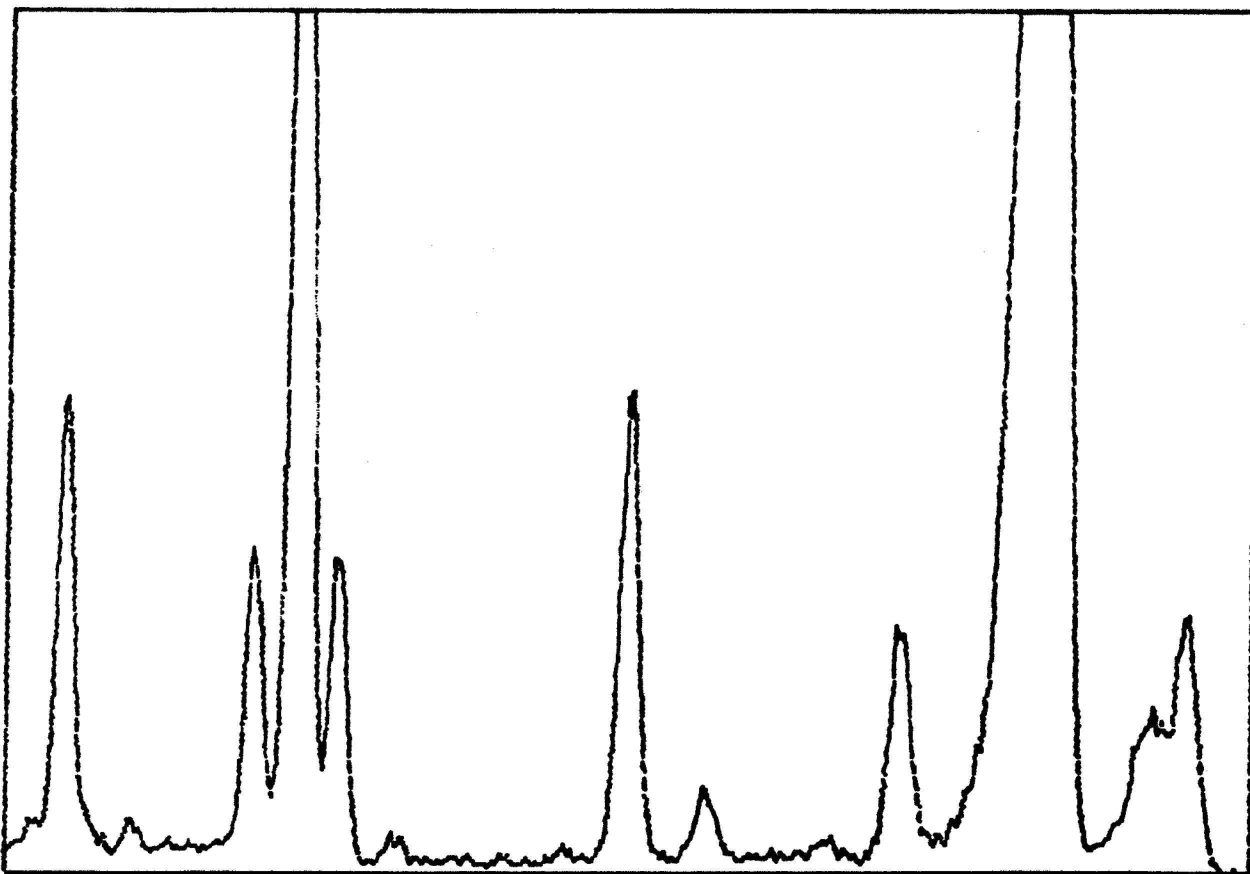
DATE : 4-5-82

VOLUME : 1777 m^3

D-S46.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (30).

QUANTEX-RAY GRAPHICS

LOCATION : JERSEY CITY

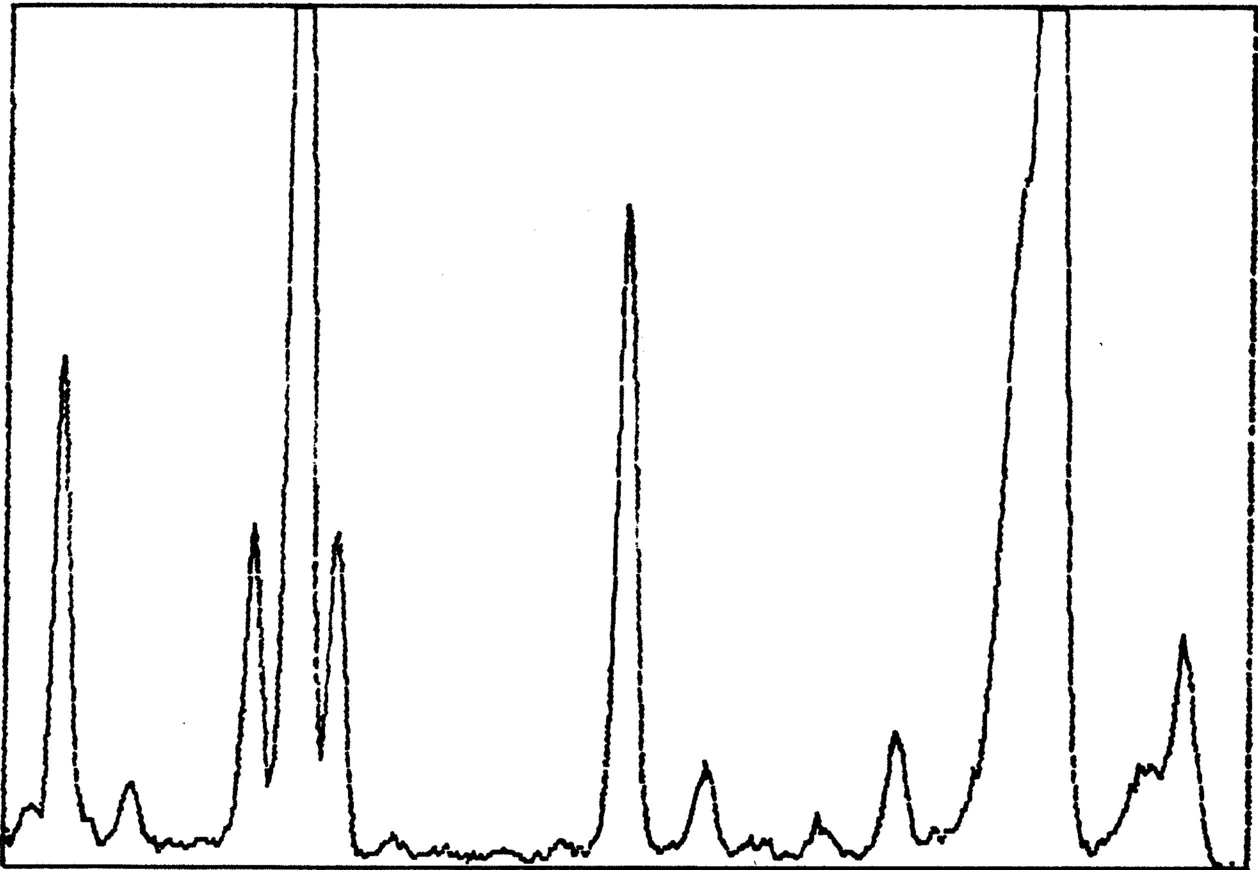
DATE : 2-4-82

VOLUME : 1739 m^3

E-015.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (31).

QUANTEX-RAY GRAPHICS

LOCATION : CHEESEQUAKE

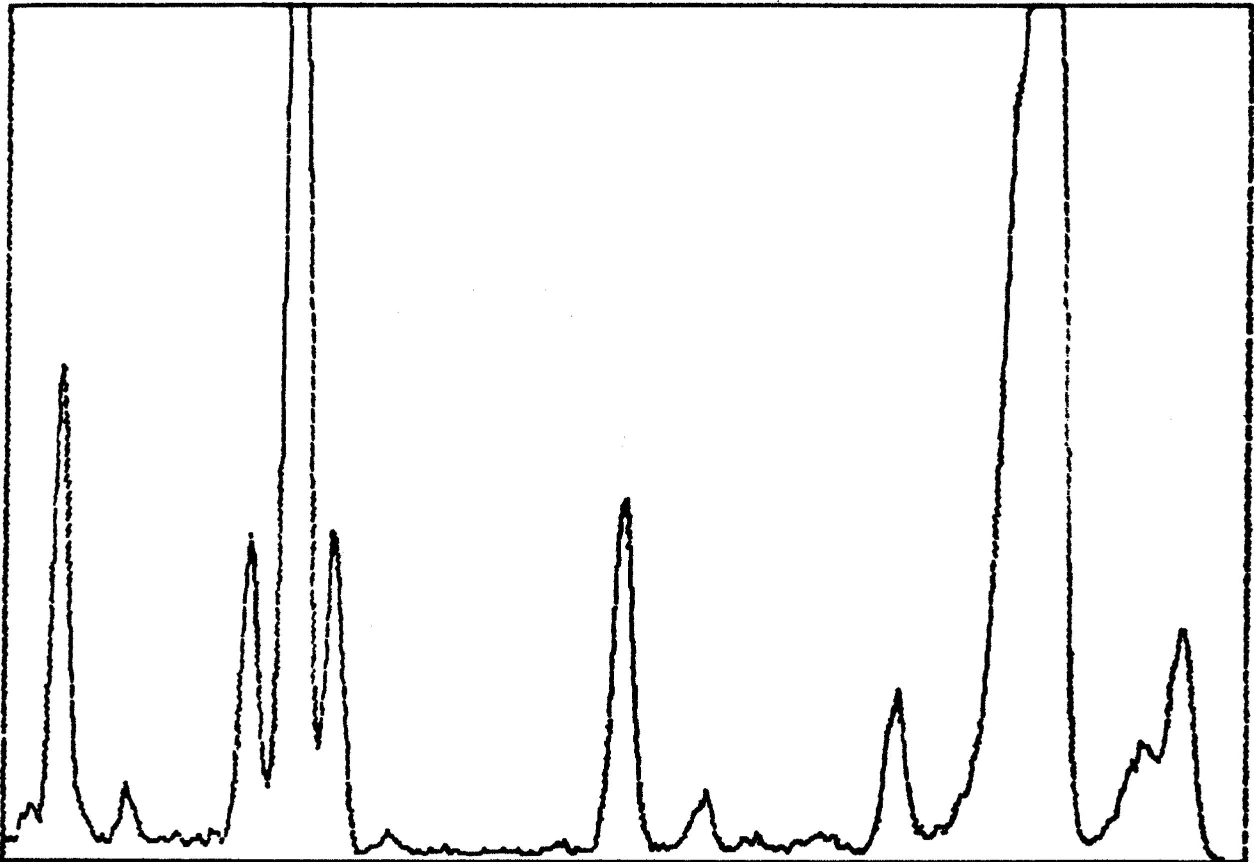
DATE : 2-4-82

VOLUME : 1890 m^3

E-S9.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (32).

QUANTEX-RAY GRAPHICS

LOCATION : METUCHEN

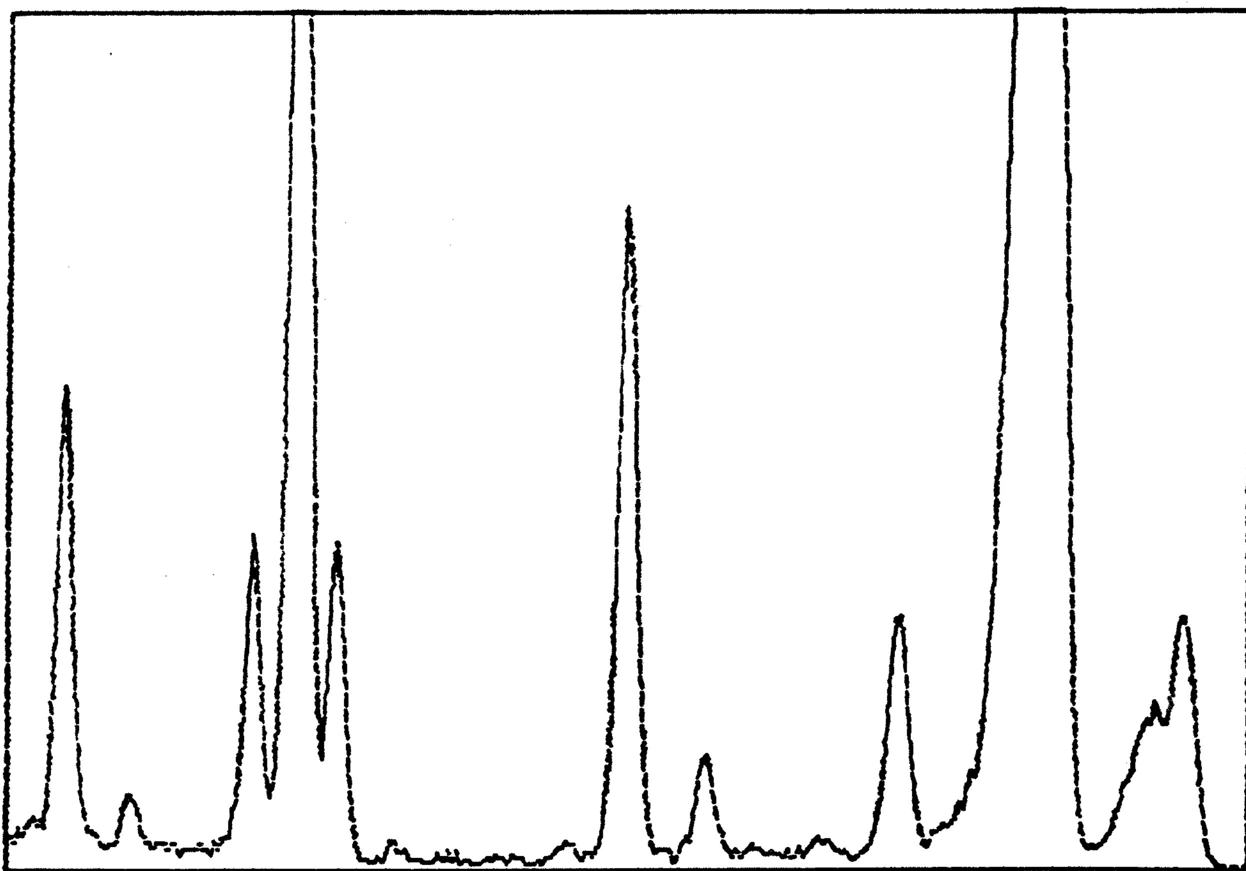
DATE : 2-4-82

VOLUME : 1878 m^3

E-S11.2

FR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (33).

QUANTEX-RAY GRAPHICS

LOCATION : PERTH AMBOY

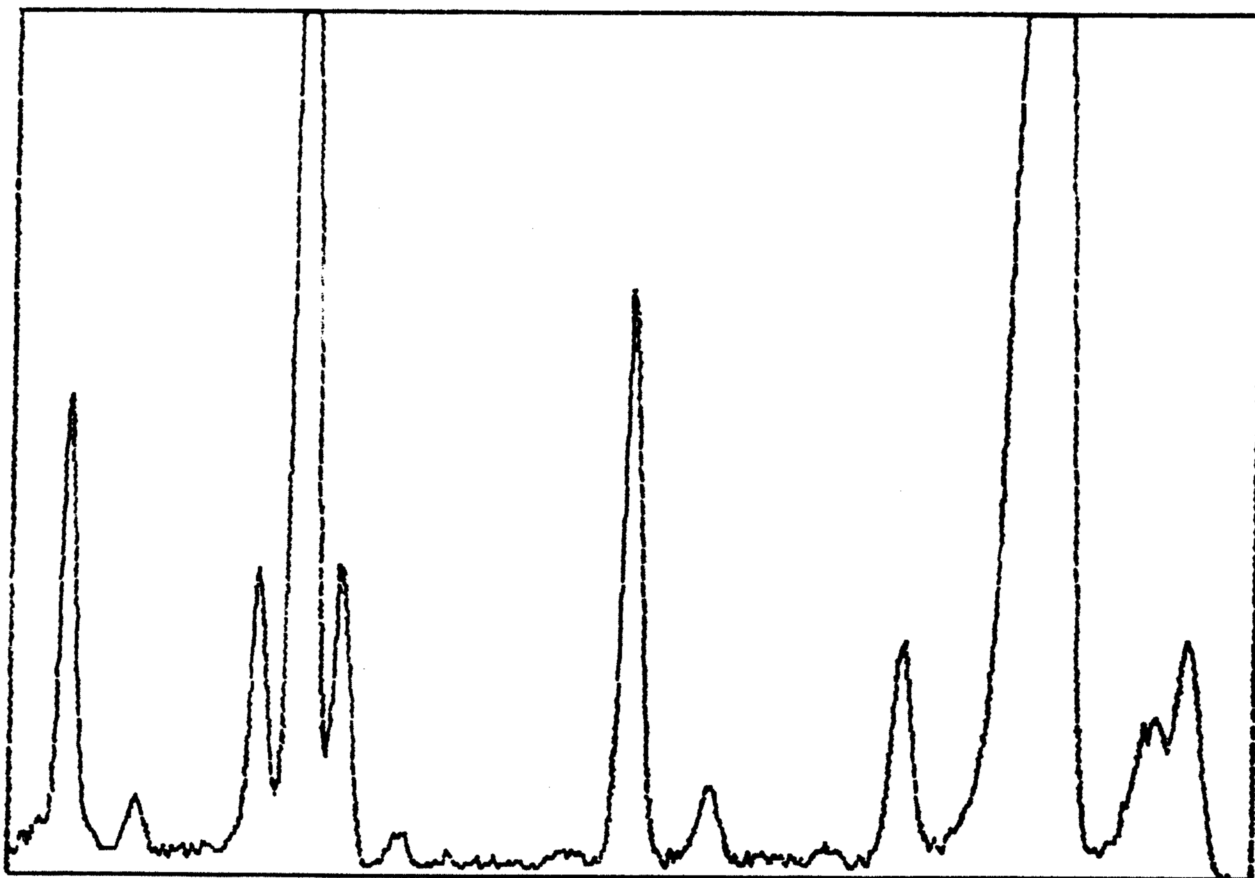
DATE : 2-4-82

VOLUME : 1881 m^3

E-S68.2

PR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (34).

B. STANDARD'S ACQUISITION.

Acquiring a standard requires the same procedure as the sample's acquisition. The urban particulate matter is placed in a plastic container and covered with a mylar film allowing the x-rays to strike the particulates through that film.

After the acquisition of the spectrum, the concentrations of the elements of interest must be saved along with the standard's ID and the indication that this spectrum is a standard.

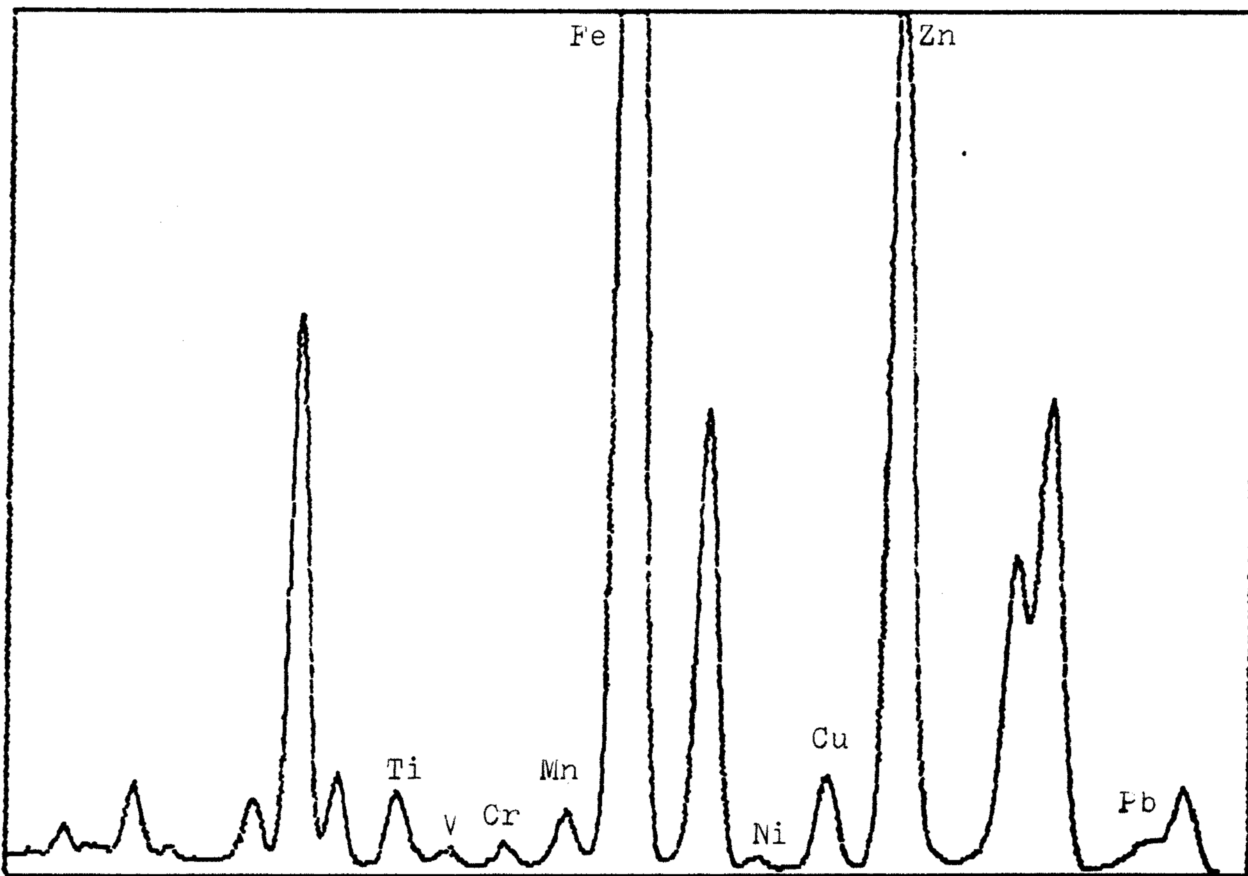
Figure (35) shows the standard's spectrum.

QUANTEX-RAY GRAPHICS

NBS-2

FR=　　　S　　　200SEC　　　　　0 INT

V=8192　H=20KEV　1:1Q　　AQ=20KEV　1Q



< 1.28KEV　　　XES　　　11.52KEV>

Figure (35)

C. ESCAPE PEAKS.

Escape peaks in a spectrum are due to lost x-ray energies that originate from the excitation of silicon atoms in the detector. When the energy from an x-ray of an element is absorbed in the detector, silicon K x-rays (Si KA=1.74 KeV) are created and reabsorbed. However, some of the Si K x-rays escape from the detector and a separate peak appears that is shifted 1.74 KeV down the energy scale from the detected parent x-ray. Most of the Si x-rays are reabsorbed in the detector, but a certain percentage escapes, resulting in a small peak appearing at 2.77 KeV (4.51 - 1.74 = 2.77). (Ti KA = 4.51 KeV).

The effect of escape peaks on a spectrum can be corrected by removing the displaced counts from the spectrum and replacing them in the parent peak. The Quantex command routine ESC obtains the intensity of the parent x-ray peak, and the counts due to the escape peaks are stripped on a channel by channel basis. When a spectrum is in memory group one and the ESC command is entered, the escape peaks in the spectrum are visibly removed and added to the parent peak.

D. BACKGROUND REMOVAL.

The background in a spectrum is defined as counts in the

spectrum which are not in the x-ray peaks of interest from the sample. The background increases the problems involved in interpreting the data, and detracts from the statistical precision of the results. There are two sources of background in x-ray spectra. The external background, which originates outside the detector, and the internal background which originates from phenomena inside the detector. The external background consists primarily of scattered radiation from the x-ray source used to excite the sample. Internal background is caused when the energy of the original x-ray is distorted from its true value.

In this analysis the background was not a major factor, as shown in figure (36), nevertheless, the spectrum of the blank filter was subtracted from the spectrum of each sample.

E. LSQ ANALYSIS.

The LSQ (least squares) quantitative program can be used to estimate the concentration of an element from the intensity of one of the element's characteristic peaks (K, L, or M). In the simplest case the concentration (C) of an element is a linear function of the measured net peak intensity (I).

$$C = A_0 + A_1 I$$

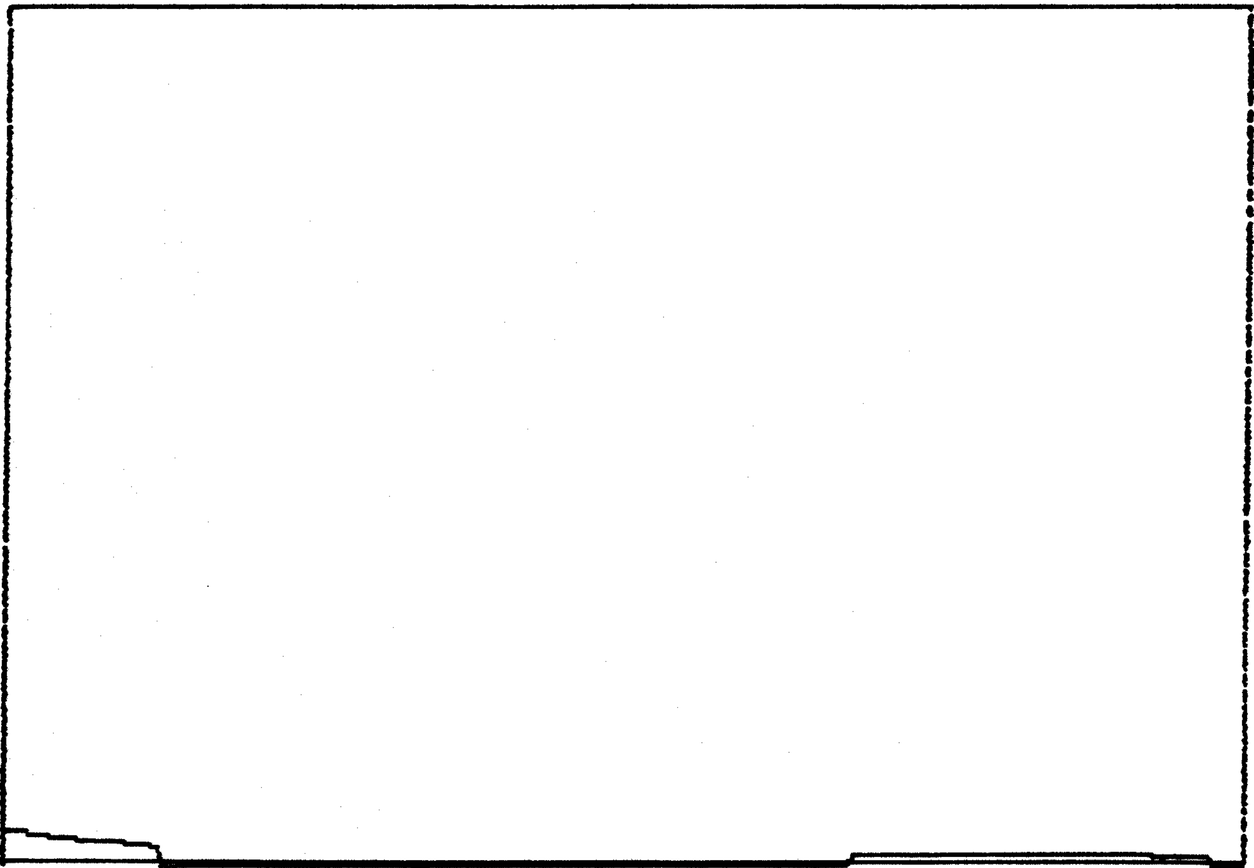
This program can also construct a quadratic calibration

QUANTEX-RAY GRAPHICS

BK1

FR= S 200SEC 0 INT

V=1024 H=20KEV 1:1Q AQ=20KEV 1Q



< 1.28KEV XES 11.52KEV>

Figure (36).

curve to fit the concentration (C) vs. intensity (I) data from known standard speciments which may fit the data.

$$C = A_0 + A_1 I + A_2 I^2$$

The least squares program (LSQ) constructs a curve based on the known concentration and intensity data from a set of standards, constructs a calibration curve for each of the elements in the standard, and determines the value of A_0, A_1, and/or A_2, depending on whether a linear or a quadratic fit is being performed. After these "best fit" values have been determined, LSQ can provide concentration results for elements in unknown samples from their measured line intensities.

The LSQ analysis performed, is outlined in the following steps.

LSQ ANALYSIS	ENTRY	SYSTEM RESPONSE
A. The spectrum to be analyzed is re-	RCL	
called and the element's list examined	ENTER	
in order to include all elements of		ID :
interest	ID	
	ENTER	
B. The command ESC is typed in order	ESC	

LSQ ANALYSIS	ENTRY	SYSTEM RESPONSE
to remove the escape peaks.	ENTER	
Note that the background has been re-		ESC
moved along with the blank filter's		REMOVED
spectrum.		
C. The command ANA is entered and	ANA	
the peaks of interest marked. The	ENTER	ENERGY
command ANA is used to synthesize		CALIBRATION
Gaussian models, in order to extract		STANDARD ?
the net peak intensities for the ele-	NO	
ments of interest.	ENTER	ANALYZING
When the procedure of analysis is com-		
pleted the system will print out the		
count rates (CTS/SEC) of the peaks of		
interest.		
D. When the printout is complete the		QUANTITATIVE
system will display the message:		RESULTS (Y/N)
Y for yes is entered if the in-	Y	
tensities are from an unknown.	ENTER	
E. Then the system will respond:		EXACT OR LSQ ?
The LSQ command is entered.	LSQ	

After the LSQ analysis of all the elements of interest is completed the system will print out the concentrations of unknowns in weight percent (wt. %). Table (VI) shows the results of airborne particulate analysis by XRF referenced against N. B. S. standards.

F. RESULTS.

Table (VI). Airborne Particulate Analysis by X-Ray Fluorescence Referenced Against NBS Standards. μg/g

SAMPLE #	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb
A-002	278	24	24	42	991	19	66	157	2658
A-005	269	26	15	53	1583	22	147	224	3579
A-040	232	22	32	43	665	20	122	97	2965
A-044	259	21	38	75	1075	19	56	78	3453
A-046	255	20	41	46	865	20	56	171	4103
A-S8	271	19	42	51	754	17	39	130	3446
A-S9	218	18	33	44	786	18	45	149	3420
A-S11	235	12	33	67	1445	17	44	156	3834
A-S12	228	17	30	99	1129	14	32	107	2450
A-S33	274	22	38	50	1019	23	1115	193	3994
A-S45	256	30	30	50	824	17	38	76	2594
A-S49	253	16	35	44	709	18	35	110	3569
A-S59	252	15	21	56	762	17	44	198	5129

Table (VI) continued.

SAMPLE #	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb
A-S68	445	22	22	68	1301	20	58	174	4126
B-015	288	18	16	45	1467	16	60	127	3371
B-S40	224	21	35	35	671	18	37	153	3975
B-S43	269	20	46	78	1576	25	165	216	2762
C-015	348	36	43	57	1499	17	78	278	4584
C-S43	263	21	29	54	825	17	47	99	3440
C-S46	239	19	25	39	569	19	45	129	3876
C-S68	429	29	30	56	1132	20	43	149	3673
D-015	362	31	42	68	1478	24	85	222	4079
D-040	330	15	30	42	1023	18	83	117	3411
D-S43	314	34	44	81	1439	21	54	252	5332
D-S46	282	17	39	42	831	16	41	142	4178
E-015	223	13	28	50	1112	20	38	72	2585
E-S9	260	10	32	40	634	20	34	101	2990
E-S11	224	17	23	52	1132	17	34	147	4183
E-S68	310	19	25	66	958	20	38	137	4092

STAT. :	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb
MEAN :	279	20.8	31.7	54.9	1043	18.9	95.8	150.3	3634
ST. DEV. :	57.2	6.3	8.3	14.9	314.1	2.5	199	52.7	721

7. ANALYSIS BY AA.

A. CONDITIONS OF ANALYSIS.

The atomic absorption analysis was performed on a Varian Techtron spectrometer. The conditions employed for analysis of each element, are listed in table (VII).

Table (VII). Conditions for AA Analysis.

ELEMENT	WAVELENGTH nm	LAMP CURRENT mA	FUEL	SENSITIVITY µg/ml
Ti	364.3	20	ACET.	1.400
V	318.5	20	ACET.	0.880
Cr	357.9	5	ACET.	0.055
Mn	279.5	5	ACET.	0.024
Fe	248.3	5	ACET.	0.062
Ni	232.0	5	ACET.	0.066
Cu	324.7	3	ACET.	0.040
Zn	213.9	5	ACET.	0.009
Pb	217.0	6	ACET.	0.110

B. STANDARDS.

The standards for the atomic absorption analysis were prepared by dissolving 1g of metal (99 % pure) in acid and di-

luting to one liter to get 1000 μg/ml metal in solution.

C. SAMPLES.

The samples were collected on a Whatman quartz microfiber filter paper with dimensions of 8 x 10 inches, or 51612.8 mm^2. The polluted filter area was 7.25 x 9.0 inches or 42096.69 mm^2. To determine the amount of particulates on each sample filter, in micrograms, the following relation is established :

$$\frac{\text{AREA OF SAMPLE}}{\text{TOTAL FILTER AREA}} \times \text{TOTAL PARTICULATES} = \text{PARTICULATES IN SAMPLE}$$

Information regarding each sample is listed in table (VIII).

Table (VIII). Data for AA Sample Analysis.

SAMPLE #	SAMPLING VOLUME m^3	PARTICULATES PER UNIT VOLUME μg/m3	TOTAL PARTICULATES IN FILTER μg	SAMPLE AREA mm^2	PARTICULATES IN SAMPLE g
A-002	1830	48	87840	7308	0.0152
A-005	1789	63	112707	7920	0.0212
A-040	1828	38	69464	7744	0.0128
A-044	1875	62	116250	7569	0.0209
A-046	1771	41	72611	8008	0.0138
A-S8	1940	39	75660	7568	0.0136
A-S9	1868	28	52304	8008	0.0100
A-S11	1864	50	93200	7656	0.0169

Table (VIII) continued.

SAMPLE #	SAMPLING VOLUME m^3	PARTICULATES PER UNIT VOLUME $\mu g/m^3$	TOTAL PARTICULATES IN FILTER μg	SAMPLE AREA mm^2	PARTICULATES IN SAMPLE g
A-S12	1921	33	63393	7830	0.0118
A-S33	1821	45	81945	6873	0.0133
A-S45	1848	36	66528	7656	0.0121
A-S49	1842	26	47892	8100	0.0092
A-S59	1857	26	48282	7832	0.0090
A-S68	1858	48	89184	7743	0.0164
B-015	1882	73	137386	7482	0.0244
B-S40	1859	25	46475	7553	0.0083
B-S43	1832	61	111752	7470	0.0198
C-015	1942	110	213620	7480	0.0379
C-S43	1812	56	101472	7654	0.0184
C-S46	1829	27	49383	7743	0.0091
C-S68	1740	61	106140	7644	0.0193
D-015	1993	89	177377	6552	0.0276
D-040	1880	34	63920	7568	0.0115
D-S43	1841	77	141757	7396	0.0249
D-S46	1777	30	53310	7735	0.0098
E-015	1739	51	88689	7560	0.0159
E-S9	1890	25	47250	7209	0.0081
E-S11	1878	31	58218	7380	0.0102
E-S68	1881	37	69597	7482	0.0124

D. RESULTS.

The results produced by atomic absorption analysis are shown in table (IX).

Table (IX). Airborne Particulate Analysis by AA. (μg/g)

SAMPLE #	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb
A-002	1772	562	866	261	10732	225	1362	2218	5982
A-005	1648	573	467	288	19139	314	3165	3936	5879
A-040	1161	494	1022	255	6212	245	2612	1524	6880
A-044	1261	457	1222	399	10760	318	958	1086	6224
A-046	1598	503	1739	322	9558	243	1152	2561	7445
A-S8	2140	463	1910	224	5785	110	623	1860	6486
A-S9	770	434	1150	335	8400	165	865	2380	6995
A-S11	964	257	1047	526	17455	198	882	2071	7050
A-S12	771	369	1102	1076	15224	88	572	1860	5000
A-S33	1440	520	1334	374	12565	376	35939	2323	7315
A-S45	1694	798	1078	413	6954	136	773	1165	6235
A-S49	1438	316	1260	268	6742	197	671	1631	5912
A-S59	1811	194	755	373	8517	89	894	2767	10200
A-S68	3619	423	604	439	13253	305	1210	2201	8597
B-015	1906	395	545	351	17446	124	1119	1815	6914
B-S40	1057	450	1201	162	6201	187	704	2876	7276

Table (IX) continued.

SAMPLE #	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb
B-S43	1663	462	2236	453	18956	426	3573	3752	6142
C-015	2701	905	1929	439	17230	164	1630	5164	9068
C-S43	1579	477	1052	372	8372	157	974	1563	7055
C-S46	1262	418	904	204	4764	245	878	1864	7120
C-S68	3768	710	1103	477	12708	261	753	2101	6684
D-015	2878	757	1864	638	17598	398	1767	3859	7375
D-040	2462	302	1119	250	11171	184	1757	1701	6171
D-S43	2239	871	2041	704	17059	281	1081	4366	10659
D-S46	1831	368	1683	273	8468	140	802	2012	7684
E-015	843	273	1016	245	11918	210	780	1053	5431
E-S9	1542	172	1129	219	5769	273	581	1617	6345
E-S11	1120	355	682	370	12703	168	636	2088	7701
E-S68	2935	350	927	625	10241	270	899	2161	7403

STAT.	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb
MEAN :	1789	469	1206	390	11445	224	2376	2295	7077
ST. DEV. :	788.	186	464.	188	4477	89	6501	999	1272

8. RESULTS AND STATISTICS.

Comparing the results that the two methods produced, it is obvious that a difference in values exists. This difference is due to a number of reasons examined in the next section. In order to understand the potential difference existing in the results the two methods produced, the following parameters were examined :

(a) The statistical information furnished by the (AA / XRF) ratio.

(b) The (AA / XRF) ratio between the two methods and for each element.

The (AA / XRF) ratio along with the statistical information is shown in table (X).

Table (X). Ratio and statistics for the two methods.

ELEMENT	AA/XRF MEAN RATIO	STD. DEVIATION	REL. S.D. %
Ti	6.24	1.64	26.20
V	22.01	2.74	12.40
Cr	37.40	5.47	14.60
Mn	6.90	1.54	22.30
Fe	10.69	1.32	12.38
Ni	11.48	3.18	27.70
Cu	19.80	1.64	8.30
Zn	15.07	1.62	10.80
Pb	1.95	0.18	9.51

In order to bridge the gap existing between the two methods, the following calculations were employed. The average value of three samples was taken as a standard. These three samples were selected on the basis of minimum possible deviation from the mean sample value, with regard to all elements, so that the statistical distribution of values remains the same.

The values produced by the three samples and for each element are shown below.

ELEMENT : Ti

SAMPLE	AA	XRF
A-046	1599	255
A-S45	1694	256
A-S59	1811	252
AVERAGE	1701.3	254.3

$$\text{FACTOR AA/XRF} = \frac{1701.3}{254.3} = 6.69$$

ELEMENT : V

SAMPLE	AA	XRF
A-046	503	20
A-S45	789	30
A-S59	194	15
AVERAGE	495.3	21.7

$$\text{FACTOR AA/XRF} = \frac{495.3}{21.7} = 22.86$$

ELEMENT : Cr

SAMPLE	AA	XRF
A-046	1739	41
A-S45	1078	30
A-S59	755	21
AVERAGE	1190.6	30.6

$$\text{FACTOR AA/XRF} = \frac{1190.6}{30.6} = 38.9$$

ELEMENT : Mn

SAMPLE	AA	XRF
A-046	322	46
A-S45	413	50
A-S59	439	68
AVERAGE	391.3	54.6

$$\text{FACTOR AA/XRF} = \frac{391.3}{54.6} = 7.16$$

ELEMENT : Fe

SAMPLE	AA	XRF
A-046	9558	865
A-S45	6959	824
A-S59	8517	762
AVERAGE	8344.6	817

$$\text{FACTOR AA/XRF} = \frac{8344.6}{817} = 10.2$$

ELEMENT : Ni

SAMPLE	AA	XRF
A-046	243	20
A-S45	136	17
A-S59	89	17
AVERAGE	156	18

$$\text{FACTOR AA/XRF} = \frac{156}{18} = 8.66$$

ELEMENT : Cu

SAMPLE	AA	XRF
A-046	1152	56
A-S45	773	38
A-S59	894	44
AVERAGE	939.6	46

$$\text{FACTOR AA/XRF} = \frac{939.6}{46} = 20.42$$

ELEMENT : Zn

SAMPLE	AA	XRF
A-046	2561	171
A-S45	1165	76
A-S59	2767	198
AVERAGE	2164.3	148.3

$$\text{FACTOR AA/XRF} = \frac{2164.3}{148.3} = 14.6$$

ELEMENT : Pb

SAMPLE	AA	XRF
A-046	7445	4103
A-S45	6235	2594
A-S59	10200	5129
AVERAGE	7960	3942

$$\text{FACTOR AA/XRF} = \frac{7960}{3942} = 2.02$$

The resulting factors (AA/XRF) for each element, produced by the samples A-046, A-S45, and A-S59 are listed in table (XI).

Table (XI). Factors Produced for each Element.

ELEMENT	FACTOR
Ti	6.69
V	22.86
Cr	38.90
Mn	7.16
Fe	10.20
Ni	8.66
Cu	20.42
Zn	14.60
Pb	2.02

These (AA/XRF) factors were then multiplied by each XRF sample value as following.

$$\frac{\mu g\ AA\ (std.)}{\mu g\ XRF\ (std.)} \times \mu g\ XRF\ (sample) = \mu g\ AA\ (sample)$$

where $\mu g\ AA\ /\ \mu g\ XRF\ (std.)$, is the factor for each element.

The final results of the analysis after the above calculations are shown in tables (XII) to (XXI).

Table (XII). Element Ti

SAMPLE #	AA CONC. WT %	XRF CONC. WT %	D %
A-002	0.177	0.186	5.1
A-005	0.165	0.180	9.1
A-040	0.116	0.155	33.6
A-044	0.126	0.173	37.3
A-046	0.160	0.170	6.2
A-S8	0.214	0.181	15.4
A-S9	0.077	0.146	89.6
A-S11	0.096	0.157	63.5
A-S12	0.071	0.152	114.1
A-S33	0.144	0.183	27.1
A-S45	0.169	0.171	1.2
A-S49	0.144	0.169	17.3
A-S59	0.181	0.168	7.2
A-S68	0.362	0.298	17.7
B-015	0.191	0.193	1.1
B-S40	0.106	0.150	41.5
B-S43	0.166	0.180	8.4
C-015	0.270	0.233	13.7
C-S43	0.158	0.176	11.4

Table (XII). Continued.

SAMPLE #	AA CONC. WT %	XRF CONC. WT %	D %
C-S46	0.126	0.160	27.0
C-S68	0.377	0.287	23.9
D-015	0.288	0.242	15.9
D-040	0.246	0.221	10.2
D-S43	0.224	0.210	6.2
D-S46	0.183	0.189	3.3
E-015	0.084	0.149	77.4
E-S9	0.154	0.174	13.0
E-S11	0.112	0.150	33.9
E-S68	0.193	0.207	29.3

STATISTICS.	AA METHOD	XRF METHOD
MEAN..........	0.178	0.186
STD.DEV.......	0.079	0.038
% DEV.........	44.2 %	20.2 %

Average difference between methods : 26.2 %

Table (XIII). Element V.

SAMPLE #	AA CONC. WT %	XRF CONC. WT %	D %
A-002	0.056	0.055	1.8
A-005	0.057	0.059	3.5
A-040	0.049	0.050	2.0
A-044	0.046	0.048	4.3
A-046	0.050	0.046	8.0
A-S8	0.046	0.043	6.5
A-S9	0.043	0.041	4.6
A-S11	0.026	0.027	3.8
A-S12	0.037	0.039	5.4
A-S33	0.052	0.050	3.8
A-S45	0.079	0.069	12.6
A-S49	0.032	0.036	12.5
A-S59	0.019	0.034	78.9
A-S68	0.042	0.050	19.0
B-015	0.039	0.042	7.7
B-S40	0.045	0.049	8.9
B-S43	0.046	0.047	2.2
C-015	0.090	0.082	8.9
C-S43	0.048	0.048	0.0

Table (XIII). Continued.

SAMPLE #	AA CONC. WT %	XRF CONC. WT %	D %
C-S46	0.042	0.044	4.8
C-S68	0.071	0.066	7.0
D-015	0.076	0.071	6.6
D-040	0.030	0.035	16.7
D-S43	0.087	0.079	9.2
D-S46	0.037	0.040	8.1
E-015	0.027	0.030	11.1
E-S9	0.017	0.024	41.2
E-S11	0.035	0.038	8.6
E-S68	0.035	0.043	22.9

STATISTICS.	AA METHOD	XRF METHOD
MEAN..........	0.047	0.048
STD. DEV......	0.018	0.014
% DEV.........	39.6 %	30.2 %

Average difference between methods : 11.4 %

Table (XIV). Element Cr

SAMPLE #	AA CONC. WT %	XRF CONC. WT %	D %
A-002	0.087	0.093	6.9
A-005	0.047	0.058	23.4
A-040	0.102	0.123	20.6
A-044	0.122	0.148	21.3
A-046	0.174	0.159	8.6
A-S8	0.191	0.163	14.7
A-S9	0.115	0.128	11.3
A-S11	0.105	0.128	21.9
A-S12	0.110	0.117	6.4
A-S33	0.133	0.147	10.5
A-S45	0.108	0.116	7.4
A-S49	0.126	0.138	9.5
A-S59	0.076	0.081	6.6
A-S68	0.060	0.085	41.7
B-015	0.054	0.062	14.8
B-S40	0.120	0.138	15.0
B-S43	0.224	0.179	20.1
C-015	0.193	0.166	14.0
C-S43	0.105	0.115	9.5

Table (XIV). Continued.

SAMPLE #	AA CONC. WT %	XRF CONC. WT %	D %
C-S46	0.090	0.097	7.8
C-S68	0.110	0.118	7.3
D-015	0.186	0.163	12.4
D-040	0.112	0.118	5.4
D-S43	0.204	0.170	16.7
D-S46	0.168	0.152	9.5
E-015	0.102	0.109	6.7
E-S9	0.113	0.125	10.6
E-S11	0.068	0.089	30.9
E-S68	0.093	0.097	4.3

STATISTICS.	AA METHOD	XRF METHOD
MEAN..........	0.121	0.123
STD. DEV......	0.046	0.033
% DEV.........	38.1 %	26.8 %

Average difference between methods : 13.6 %

Table (XV). Element Mn

SAMPLE #	AA CONC. WT %	XRF CONC. WT %	D %
A-002	0.026	0.030	15.4
A-005	0.029	0.038	31.0
A-040	0.025	0.031	24.0
A-044	0.040	0.053	32.5
A-046	0.032	0.033	3.1
A-S8	0.022	0.036	63.6
A-S9	0.033	0.031	6.1
A-S11	0.053	0.048	9.4
A-S12	0.107	0.071	33.6
A-S33	0.038	0.036	5.3
A-S45	0.041	0.036	12.2
A-S49	0.027	0.032	18.5
A-S59	0.037	0.040	8.1
A-S68	0.044	0.051	15.9
B-015	0.035	0.038	8.6
B-S40	0.016	0.025	56.2
B-S43	0.045	0.056	24.4
C-015	0.044	0.041	6.8
C-S43	0.037	0.039	5.4

Table (XV). Continued.

SAMPLE #	AA CONC. WT %	XRF CONC. WT %	D %
C-S46	0.020	0.028	40.0
C-S68	0.048	0.040	16.7
D-015	0.064	0.049	23.4
D-040	0.025	0.030	20.0
D-S43	0.070	0.058	17.1
D-S46	0.027	0.030	11.1
E-015	0.025	0.036	44.0
E-S9	0.022	0.029	31.8
E-S11	0.037	0.037	0.0
E-S68	0.062	0.047	24.2

STATISTICS	AA METHOD	XRF METHOD
MEAN...........	0.039	0.040
STD. DEV.......	0.019	0.011
% DEV..........	47.9 %	26.8 %

Average difference between methods : 21.0 %

Table (XVI). Element Fe

SAMPLE #	AA CONC. Wt %	XRF CONC. Wt %	D %
A-002	1.073	1.011	5.8
A-005	1.913	1.615	15.6
A-040	0.621	0.678	9.2
A-044	1.076	1.096	1.8
A-046	0.956	0.882	7.7
A-S8	0.578	0.769	33.0
A-S9	0.840	0.802	4.5
A-S11	1.745	1.474	15.5
A-S12	1.522	1.152	24.3
A-S33	1.256	1.039	17.3
A-S45	0.696	0.841	20.8
A-S49	0.674	0.723	7.3
A-S59	0.852	0.777	8.8
A-S68	1.325	1.327	0.2
B-015	1.745	1.496	14.3
B-S40	0.620	0.684	10.3
B-S43	1.897	1.606	15.3
C-015	1.723	1.529	11.3
C-S43	0.837	0.841	0.5

Table (XVI). Continued.

SAMPLE #	AA CONC. WT %	XRF CONC. WT %	D %
C-S46	0.476	0.580	21.8
C-S68	1.271	1.154	9.2
D-015	1.760	1.507	14.4
D-040	1.117	1.043	6.6
D-S43	1.706	1.468	13.9
D-S46	0.847	0.848	0.1
E-015	1.192	1.134	4.9
E-S9	0.570	0.647	13.5
E-S11	1.270	1.154	9.1
E-S68	1.024	0.977	2.6

STATISTICS	AA METHOD	XRF METHOD
MEAN...........	1.144	1.064
STD. DEV.......	0.448	0.320
% DEV..........	39.2 %	30.1 %

Average difference between methods : 11.0 %

Table (XVII). Element Ni

SAMPLE #	AA CONC. WT %	XRF CONC, WT %	D %
A-002	0.0225	0.0165	26.7
A-005	0.0314	0.0191	39.2
A-040	0.0245	0.0170	30.6
A-044	0.0318	0.0165	48.1
A-046	0.0243	0.0173	28.8
A-S8	0.0110	0.0147	33.6
A-S9	0.0165	0.0156	5.5
A-S11	0.0198	0.0147	25.8
A-S12	0.0088	0.0121	37.5
A-S33	0.0376	0.0199	47.1
A-S45	0.0136	0.0147	8.1
A-S49	0.0197	0.0158	19.8
A-S59	0.0089	0.0147	65.2
A-S68	0.0305	0.0173	43.3
B-015	0.0124	0.0140	12.9
B-S40	0.0187	0.0158	15.5
B-S43	0.0426	0.0215	49.5
C-015	0.0164	0.0150	8.5
C-S43	0.0157	0.0148	5.7

Table (XVII). Continued.

SAMPLE #	AA CONC. WT %	XRF CONC. WT %	D %
C-S46	0.0245	0.0170	30.6
C-S68	0.0261	0.0174	33.3
D-015	0.0398	0.0208	47.7
D-040	0.0184	0.0155	15.8
D-S43	0.0281	0.0179	36.3
D-S46	0.0140	0.0144	2.9
E-015	0.0210	0.0174	17.1
E-S9	0.0273	0.0177	35.2
E-S11	0.0168	0.0151	10.1
E-S68	0.0270	0.0173	35.9

STATISTICS	AA METHOD	XRF METHOD
MEAN............	0.0224	0.0164
STD. DEV........	0.0089	0.0021
% DEV...........	39.7 %	12.8 %

Average difference between methods : 28.1 %

Table (XVIII). Element Cu.

SAMPLE #	AA CONC. WT %	XRF CONC. WT %	D %
A-002	0.136	0.135	0.7
A-005	0.316	0.300	5.1
A-040	0.261	0.449	72.0
A-044	0.095	0.114	20.0
A-046	0.115	0.114	0.9
A-S8	0.062	0.079	27.4
A-S9	0.087	0.092	5.7
A-S11	0.088	0.090	2.3
A-S12	0.057	0.065	14.0
A-S33	3.593	2.277	36.6
A-S45	0.077	0.077	0.0
A-S49	0.067	0.072	7.5
A-S59	0.089	0.089	0.0
A-S68	0.121	0.118	2.5
B-015	0.121	0.122	0.8
B-S40	0.070	0.075	7.1
B-S43	0.357	0.337	5.6
C-015	0.163	0.160	1.8
C-S43	0.097	0.097	0.0

Table (XVIII). Continued.

SAMPLE #	AA CONC. WT %	XRF CONC. WT %	D %
C-S46	0.088	0.093	5.7
C-S68	0.075	0.087	16.0
D-015	0.177	0.173	2.3
D-040	0.175	0.169	3.4
D-S43	0.108	0.110	1.9
D-S46	0.080	0.084	5.0
E-015	0.078	0.087	11.5
E-S9	0.058	0.069	19.0
E-S11	0.064	0.070	9.4
E-S68	0.090	0.078	13.3

STATISTICS	AA METHOD	XRF METHOD
MEAN............	0.119	0.122
STD. DEV........	0.077	0.069
% DEV...........	64.7 %	56.5 %

Average difference between methods : 10.3 %

NOTE : SAMPLE # A-S33 WAS EXCLUDED.

Table (XIX). Element Zn.

SAMPLE #	AA CONC. WT %	XRF CONC. WT %	D %
A-002	0.222	0.229	3.2
A-005	0.393	0.327	16.8
A-040	0.152	0.141	7.2
A-044	0.109	0.114	4.6
A-046	0.256	0.249	2.7
A-S8	0.186	0.190	2.2
A-S9	0.238	0.217	8.8
A-S11	0.207	0.226	9.2
A-S12	0.186	0.156	16.1
A-S33	0.232	0.282	21.6
A-S45	0.116	0.111	4.3
A-S49	0.163	0.161	1.2
A-S59	0.276	0.289	4.7
A-S68	0.220	0.254	15.5
B-015	0.181	0.185	2.2
B-S40	0.198	0.223	12.6
B-S43	0.375	0.315	16.0
C-015	0.515	0.406	21.2
C-S43	0.156	0.144	7.7

Table (XIX). Continued.

SAMPLE #	AA CONC. WT %	XRF CONC. WT %	D %
C-S46	0.186	0.188	1.1
C-S68	0.210	0.217	3.3
D-015	0.386	0.324	16.1
D-040	0.170	0.171	0.6
D-S43	0.437	0.368	15.8
D-S46	0.201	0.207	3.0
E-015	0.105	0.105	0.0
E-S9	0.162	0.147	9.3
E-S11	0.209	0.205	1.9
E-S68	0.216	0.200	7.4

STATISTICS	AA METHOD	XRF METHOD
MEAN...........	0.230	0.219
STD. DEV.......	0.099	0.077
% DEV..........	43.4 %	35.1 %

Average difference between methods : 8.1 %

Table (XX). Element Pb

SAMPLE #	AA CONC. WT %	XRF CONC. WT %	D %
A-002	0.598	0.537	10.2
A-005	0.588	0.723	22.6
A-040	0.688	0.599	12.9
A-044	0.622	0.697	12.1
A-046	0.744	0.829	11.4
A-S8	0.648	0.696	7.4
A-S9	0.699	0.691	1.1
A-S11	0.705	0.774	9.8
A-S12	0.500	0.495	1.0
A-S33	0.731	0.806	10.3
A-S45	0.623	0.524	15.9
A-S49	0.591	0.721	22.0
A-S59	1.020	1.036	1.6
A-S68	0.860	0.833	3.1
B-015	0.691	0.681	1.4
B-S40	0.728	0.803	10.3
B-S43	0.614	0.558	9.1
C-015	0.907	0.926	2.1
C-S43	0.705	0.695	1.4

Table (XX). Continued.

SAMPLE #	AA CONC. WT %	XRF CONC. WT %	D %
C-S46	0.712	0.783	10.0
C-S68	0.668	0.742	11.1
D-015	0.737	0.824	14.2
D-040	0.617	0.689	11.7
D-S43	1.066	1.077	1.0
D-S46	0.768	0.844	9.9
E-015	0.543	0.522	3.9
E-S9	0.634	0.604	4.7
E-S11	0.770	0.845	9.7
E-S68	0.741	0.826	11.5

STATISTICS	AA METHOD	XRF METHOD
MEAN..........	0.707	0.737
STD. DEV......	0.127	0.144
% DEV.........	17.9 %	19.5 %

Average difference between methods : 8.7 %

9. DISCUSSION.

The determination of the composition of airborne particulate matter is a major task. The general requirements imposed on the analytical methods are typical ; the multielement composition must be determined accurately and precisely over a wide concentration range. These results are to be generated by the analytical method even though there may be major variations in the general composition of the particulate samples or in their preparative histories. This is the case of the comparison attempted in this thesis. A number of particulate samples collected in the New Jersey area were analyzed by Atomic Absorption and X-ray fluorescence spectroscopy. The samples analyzed by AA were digested in acid resulting a solution of particulates. They were also measured against standard solutions of known and similar concentrations. In the XRF analysis the standards used were of different composition and with a "fixed" known concentration. The particulate samples were matched against the fixed value regardless of the differences in concentration and composition of the standard. The result of this analysis was a good distribution of values only when the compared concentration

values were similar.

Another point of interest is that XRF performs simultaneous multielement analysis with the result of interelement effects. Such effects are matrix factors which affect the determination of elements adjacent in the periodic table, especially when these elements have a large difference in concentration. This is the case of Fe KB1 lines overlapping heavily the Co KA1 lines.

The results obtained from the two methods did not match, but the ratio produced from the values of the two methods and for each element was fairly constant. This ratio allowed the two methods to bridge the gap and yield acceptable results by the introduction of empirical factors for each element.

Table (XXI) shows a statistical comparison of values attempted in order to derive the following conclusions.

(1) Samples with difference greater than 50 % from the mean sample value are very few, numbering from none to two for each element, except Ti, which has four bad matched samples. The individual samples with poor (>50 %) matches between AA and XRF methods, have also great difference between the samples and standards. They all (except one Cu sample) are

Table (XXI). Summary of Comparison.

ELEMENTS	NUMBER OF SAMPLES WITH >50% DIFFER. OF AA AND XRF	AVERAGE OF ALL AA SAMPLES WT.%	AVERAGE OF ALL XRF SAMPLES WT.%	AVERAGE DIFF. % BETWEEN AA AND XRF FOR ALL SAMPLES	AVERAGE OF BAD MATCHED SAMPLES WT.% (AA)	AVERAGE OF AA STANDARDS WT.%	% DIFF. BETWEEN STDS. & SAMPLES AVERAGE CONC.	% DIFF. BETWEEN STDS. & SAMPLES FOR BAD MATCHES	REL. ST. DEV. FOR ALL AA SAMPLES
Ti	4	0.1780	0.1860	26.2	0.0820	0.1701	5	52	44
V	1	0.0470	0.0480	11.4	0.0170	0.0495	5	65	40
Cr	0	0.1210	0.1230	13.6	-	0.1190	7	-	38
Mn	2	0.0390	0.0400	21.0	0.0190	0.0391	0.2	51	48
Fe	0	1.1440	1.0640	11.0	-	0.8344	4	-	39
Ni	1	0.0224	0.0164	28.1	0.0089	0.0156	43	43	40
Cu	1	0.1190	0.1220	10.3	0.2610	0.0939	26	178	64
Zn	0	0.2300	0.2190	8.1	-	0.2164	8	-	43
Pb	0	0.7070	0.7370	8.7	-	0.7960	8.7	-	17

between 43 to 65 % lower than the standards, while the standards are, on average, 1 to 26 % different from samples. (except Ni where standards are 43 % lower than samples).

(2) The element with the worst overall agreement (Ni) also had worst match of average sample and average standard. (43% difference).

(3) Cu sample A-040 does not follow the pattern of being lower than the standard. It is a "bad match" with relative standard deviation of 72 % . while sample A-S33 which is much higher than the standard agrees fairly well with a relative standard deviation of 36.6 % .

(4) The overall variability of the samples as expressed by the relative standard deviation is not related to the agreement between AA and XRF methods, because the elements which varied most in samples are not those with the poorest agreement.

The average difference between AA and XRF methods for all elements is between 8.1 to 28 % , while the relative standard deviation varies from 17 to 64 % .

Besides the above statistical comparison, the major point made by the present study is the following : Typical air samples with a very thin layer of particulates on them, were

analysed by XRF. These samples were compared to a standard, composed of a thick layer of airborne particulate matter of known concentration. The results of this XRF analysis were 2 to 40 times lower than the AA results of the same air samples. This difference is caused by the different amount of material in the samples and the standard.

When the same samples were compared to typical air samples taken as standards with known concentrations. (from AA analysis) the results were satisfactory and the two methods displayed an average difference of 8.1 to 28 % which is acceptable. This average difference between AA and XRF can be reduced even more if the number and the composition variability of standards is expanded. This way, air samples can be compared not only to a larger number of standards but to specific and relative standards for a better match. This was proven by the study of the deviation values which varied according to the difference between samples and standards.

To resolve the problem and minimize the factor it is necessary to consider the following steps for the XRF method.

(a) A serious need exists for more primary metal standards tailored for specific analytical techniques. The preparation and documentation of a wide variety of metal standards pro-

vides the most useful way to standardize data.

(b) A spectral library with a large variety of samples and concentrations can help to categorize and standardize a sample against the proper standard before the quantitative analysis is taken place. This can be possible with a technique called Q-Match routine. This technique accesses computer files of standard spectra so that suitable spectra can be matched to an unknown sample.

(c) The sample collection media used should be selected on the basis of low blank and minimal sample handling criteria, to avoid sample contamination and analyte loss problems.

10. CONCLUSION.

Future developments in atmospheric particulate analysis should be directed at simultaneous multielement analysis systems.

X-ray fluorescent spectroscopy was used to measure airborne particulate concentrations. The results obtained were fairly accurate even though the need to establish factors was necessary.

Further work can assure the utility of the XRF spectroscopy, using as a basis the present thesis. The samples analysed can help to create a spectral "library" if they are used as standards along with the Q-Match routine.

It is my view that XRF spectroscopy (with consideration to the above discussion) along with ICP-OES, constitute the future of environmental quantitative and qualitative ana-analysis.

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