0 0 0 0 4 9 0 1 8 7 3

UC-11, UC-37, UC-41

Submitted to American Laboratory

LBL 6878

c.1

RECEIVED
LAWRENCE
BERKELEY LABORATORY

AUG 30 1978

LIBRARY AND
DOCUMENTS SECTION

For Reference

Not to be taken from this room

Energy and Environment Division

A Survey of Instrumentation Used for Monitoring Metals in Water

Mary S. Quinby-Hunt

June, 1978

Lawrence Berkeley Laboratory University of California/Berkeley

Prepared for the U.S. Department of Energy under Contract No. W-7405-ENG-48

LBL 6878
c.1

LEGAL NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the Department of Energy, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

0 0 0 0 4 9 0 1 8 7 4

A Survey of Instrumentation Used for Monitoring Metals in Water

Environmental quality control is essential to our health and well-being. In the past decade, it has become clear that even trace and ultratrace quantities of certain pollutants can be detrimental. Numerous sophisticated techniques and instruments have been developed in order to detect, characterize and monitor these pollutants. To aid laboratories in choosing among the instrumentation and techniques available to help them understand the substances they are analyzing, and to bring them up-to-date on new developments regarding instrumentation and developing techniques, Lawrence Berkeley Laboratory has conducted, for the past few years, a Survey of Instrumentation for Environmental Monitoring.[1] Instrumental methods covered are those suitable for examining the environmental quality of Air and Water, methods used in measuring Radiation and in making Biomedical measurements. The findings of this Survey are published in volumes under the above designations.

As part of the overall Survey, a study has recently been conducted of instrumentation used to determine metals in water. Several of the techniques most commonly used for analysis and routine determinations of metals in water are shown in Table 1. They are atomic absorption spectroscopy, both flame and flameless, atomic emission spectroscopy using conventional flame sources and inductively-coupled plasma sources, and ultraviolet-visible absorption techniques. Other less frequently employed methods are X-ray fluorescence analysis using both photon and

Table 1. Some selected instrumental methods commonly used for determining metals in water

Atomic Absorption (AAS)	Flame Flameless
Atomic Emission (AES)	Conventional sources Inductively coupled plasma (ICP) sources
Ultraviolet-visible (UV-VIS) Absorption Spectrometry	
X-ray Fluorescence Spectrometry (XRF)	Photon excitation ($h\nu$) Charged particle excitation (PIXE) Energy-dispersive (ED) Wavelength-dispersive (λD)
Neutron Activation Analysis (NAA)	
Anodic Stripping Voltammetry (ASV)	

0 0 0 0 4 9 0 1 8 7 5

charged particle excitation (PIXE) with energy-dispersive and wavelength-dispersive spectral analysis. Also occasionally used are electrochemical techniques such as anodic stripping voltammetry, and activation methods using neutrons and charged-particles.

When choosing an instrumental technique to monitor or analyze for metals in water, it is essential to consider its advantage and disadvantage with respect to the particular task at hand. Before deciding, the analytical lab should consider the purpose, scope and requirements of the project. Important factors to be considered are whether the instrument is to be used for a routine, repetitive regulatory function or for research, which requires a more flexible instrument, or whether the technique must be used for quantitative determinations, qualitative determination or speciation. Speciation, the determination of the form of the metal present, is becoming increasingly important, since often one form of a metal is found to be more detrimental than another (the most obvious case being the extreme toxicity associated with certain organic mercury compounds). One must also consider the time and expertise required in making determinations, the sensitivity, accuracy and precision necessary and the expense of the technique in terms of time, personnel and equipment cost.

This paper will first briefly describe the principles of operation and the capabilities of each of the techniques listed in Table 1. The techniques will then be compared and considered in relation to a variety of water quality criteria.

Instrumental Techniques--Principles of Operation

Atomic Absorption Spectroscopy

Atomic absorption spectroscopy is based on the principle that metal atoms absorb radiation at frequencies which are characteristic of a particular metal, the amount of light being absorbed a function of its concentration. When a metal, M, in the gas phase is exposed to a source of radiation, whose photon energy, $h\nu$, corresponds to the energy difference between the atomic energy levels of the metal, light may be absorbed:

$M + h\nu \rightarrow$ absorption.

In practice, a solution containing the analyte metal (M) is atomized either by nebulization followed by atomization in a flame, or by means of a flameless device such as a graphite furnace in which the solution is dried, ashed or charred and then atomized. Light from a radiation source is passed through the vapor into a monochromator, where it is dispersed into its component wavelengths and then directed, sequentially, onto a detector (Figure 1).

Two types of radiation sources are commonly used: discrete and continuum sources. Most common discrete sources are hollow cathode lamps (HCL) or electrodeless discharge lamps (EDLs) which emit only the spectrum of the metal or metals from which they are made. With EDLs and HCLs, it is only possible to determine one or two elements at a time (depending on the number of channels in the instrument). To determine another element it is usually necessary to change the source lamp. Continuum sources, such as D_2 lamps, are less frequently used. When using continuum sources, it is not necessary to change lamps to determine a number of metals sequentially; however, currently, the low sensitivity

obtained with continuum sources, and a number of other technical problems, make the use of HCLs and EDLs the more commonly used technique.[2]

AAS is a widely applicable and sensitive technique. Table 2 lists the metals and metalloids for which AAS is the technique recommended by the EPA.[3]* Table 2 also shows the minimum detection limits for those metals reported by a variety of manufacturers of AAS instruments. It is clear from the table that the flameless techniques are far more sensitive than the flame techniques but that the flame technique is still sensitive for many metals. Flameless techniques have become more practical in the past few years, particularly with the development of the automatic sipper which reproducibly pipettes an exact amount of solution into the furnace. With human operators, there was often a substantial variability in the size of the sample pipetted and its position within the tube.

Current atomic absorption instruments available are relatively easy to operate and are readily automated. Many have options for background correction using both single beam and double beam techniques. Today microprocessor controlled instruments perform much of the tedious calibration, zeroing, and concentration calculation; in some cases even instrument diagnostics are made. The cost involved is usually moderate for an AA spectrometer with minimal instruments costing from $6,000.

AAS is particularly useful for routine, repetitive, quantitative analyses of an established set of metals. With current instrumentation

---

*Techniques recommended by the EPA as "standard methods" must be used by laboratories monitoring water who report to the EPA, unless they have had an alternative method approved. Alternative methods must be shown by each reporting laboratory to produce results equivalent to, or better than, those achieved by using the standard method. The most common texts for standard methods are Refs. 4, 5.

the method is not useful for qualitative analyses or simultaneous multi-element determinations. Without chemical pretreatment and separation, AAS cannot be used for speciation.

For more detailed information on AAS, the interested reader is referred to the excellent texts by Kirkbright and Sargent,[2] and Willard, Merritt, and Dean,[6] and Veillon.[7] There is an extensive section on atomic spectrometry in the Survey.[1] The latter includes instrument notes for commercially available instrumentation.

Atomic Emission Spectrometry

Atomic emission spectrometry (AES) is based on the principle that a metal atom in a vapor which has been excited can decay to a lower energy state by radiating light:

$$M^* \rightarrow M + h\nu$$

The frequency of the radiation emitted is characteristic of the metal atom and its intensity proportional to the concentration of the metal atom in the vapor.

As in AAS, a solution containing the analyte metal is atomized using any one of a variety of processes. Conventional flame AES uses a nebulizer and flame arrangement similar to that described above for AAS. During atomization a finite but small number of atoms are raised to an excited state, increasing the sensitivity of the technique, higher energy excitation sources have been applied, particularly inductively-coupled plasma (ICP) sources.

The light emitted from the excited metal atoms is directed into a spectrometer and in turn on to a detector. Two types of spectrometers are currently used: a monochromator which sequentially directs the

dispersed wavelengths onto a detector (Figure 2a), and a polychromator which disperses the wavelengths of light onto an array of detectors (Figure 2b).

AE spectrometers using a monochromator can be effectively used for qualitative and quantitative analyses; however, it is not possible to use such an instrument for simultaneous multielement determination. Perhaps the greatest advantage to the AES coupled to a polychromator is its ability to perform simultaneous multielement determination. Some manufacturers provide instruments which can handle as many as 50 elements, but using a polychromator, it is only possible to perform qualitative analyses for those metals which are represented in the detector array. It is not possible to determine the form of the metal present using AES with a polychromator or monochromator. Many manufacturers of AE spectrometers using an ICP source provide a scanning monochromator as an option; this allows the analyst the flexibility of the monochromator with the speed of the polychromator. The major disadvantages to the technique are the cost and size of the instruments. A minimal instrument with ten channels often costs more than $45,000. As is clear from comparing Table 3, which gives the minimum detection limits for ICP-AES instrumentation, with Table 2, the sensitivity of ICP-AES is somewhat less than that of atomic absorption techniques.

AES using an ICP source is gaining acceptance, although it has not yet been listed by the EPA as a standard method. At least one ICP-AES is currently in use in the EPA lab in Chicago, which has had the instrument approved for their lab as an alternative method.

For more detailed information on AES the reader is referred to Ref. 7.

Table 2. Detection limits reported by a variety of manufacturers for their atomic absorption instrumentation

Detection Limits (μg/ℓ)			Detection Limits (μg/ℓ)		
Metal[a]	Flame[b]	Flameless[e]	Metal	Flame[b]	Flameless[e]
Aluminum	20-50	0.4-1.0	Nickel	7-20	0.25-10
Antimony	30-100[c] 6[d]	0.8-2	Osmium	200	—
Arsenic	200-400[c] 0.1-1	0.6-7.5	Palladium	20-25	1.4-2
Barium	15-30	0.04-10	Platinum	50-100	4.5-5
Beryllium	1-5	0.01-0.3	Potassium	1-5	-0.1
Cadmium	0.15-2	0.01-0.04	Rhodium	6-10	—
Calcium	1-2	-0.03	Ruthenium	80-200	—
Chromium	3-8	0.05-1	Selenium	80-250[c] 0.2-1[d]	0.6-5
Cobalt	3-15	0.3-4	Silver	1-3	0.015-0.05
Copper	2-5	0.08-0.5	Sodium	0.3-1.0	-0.01
Gold	9-30	0.1-1	Thallium	20-70	-0.3
Iridium	1200	—	Tin	20-200	0.5-10
Iron	3-10	0.03-0.25	Titanium	60-150	3.3-100
Lead	10-30	0.15-5	Vanadium	20-160	1.5-50
Magnesium	0.1-0.3	0.003-0.3	Zinc.	0.6-3	-0.01
Manganese	3-8	0.02-0.1			
Mercury	0.1-0.5[d]	6			
Molybdenum	10-40	0.6-5			

[a]Metals or metalloids for which AA is specified as a Standard Method in 40 CFR 136.

[b]Jarrell-Ash Instrumentation Lab., Perkin Elmer, and Varian, Manufacturers Specifications, 1977.

[c]Normal flame AA; [d]hydride generation; [e]based on a 10 μℓ sample.

0 0 0 0 4 9 0 1 8 7 8

Table 3. Detection limits reported by a variety of manufacturers for atomic emission spectrometers using inductively coupled plasma sources

Metal[a]	Detection Limit (μg/ℓ)[b]	Metal	Detection Limit (μg/ℓ)
Aluminum	7-15	Nickel	6-19
Antimony	30-60	Osmium	200
Arsenic	20-330	Palladium	40
Barium	0.02-5	Platinum	20-30
Beryllium	0.02-8	Potassium	125-260
Boron	5	Rhodium	20-30
Cadmium	1-5	Ruthenium	60-5000
Calcium	0.09-4	Selenium	20-93
Chromium	1.8-6	Silver	4-15
Cobalt	2-5	Sodium	1-75
Copper	1-2	Thallium	75-1000
Gold	5	Tin	6-70
Iridium	70-100	Titanium	0.5-5
Iron	0.45-3	Vanadium	1.3-5
Lead	20-50	Zinc.	2-10
Magnesium	0.05-50		
Manganese	0.2-0.5		
Mercury	13-200		
Molybdenum	5-22		

[a]Metals or metalloids are those for which either AA or uv-vis (colorimetric)techniques are recommended by the EPA in 40 CFR 136.

[b]Applied Research Labs, Jarrell Ash, and Labtest Equipment, Manufacturers' Specifications, 1977.

Table 4. Minimum detectable limits for metals using UV-visible spectrometry

Metal[a]	Complexing Agent[b]	λ(nm)[b]	Minimum detectable limit (μg)[b]
Aluminum	Eriochrome Cyanine R	535	6[c]
Arsenic	Silver Diethyldithiocarbamate	535	1
Beryllium	Aluminon	515.5	5[c]
Boron	Curcumin	540	0.2
Cadmium	Dithizone	515	0.5
Chromium	Diphenylcarbazide	540	—
Copper	Neocuproine	457	3
Iron	Phenanthroline	510	50
Lead	Dithizone	520	—
Manganese	Persulfate/Periodate	525	5
Nickel	Heptoxime	445	—
Potassium	Cobaltinitrite	425	500
Silica	Molybdosilicate	410	1000
Silver	Dithizone	620	0.2
Vanadium	Gallic Acid	415	0.025
Zinc	Dithizone	535	1

[a]40 CFR 136. Metals listed are those for which colorimetric techniques are standard methods.

[b]Reference 4.

[c]μg/ℓ.

[d]depending on the size sample takes

Ultraviolet-Visible Absorption Spectrometry

UV-visible spectrometry is perhaps the oldest technique still widely used for the determination of metals in water. The analyte metal or metal ion is converted to a complex which has a strong molecular absorption in the UV-vis. The concentration of the metal complex is then directly related to the absorption of the solution determined by a standard UV-vis or visible spectrometer.

This technique is recommended by the EPA[3] for determination of fewer metals than is AAS. The metals for which colorimetric techniques are recommended are listed in Table 4 as are the complexing agents which are recommended for each metal. Also, the detection limits which have been reported using this technique are shown.

The advantages to this technique are its ease of operation and maintenance, as well as low cost of the instruments involved. There are several disadvantages. It is necessary to convert all the metal species to the one(s) which will react to form the correct complex, although the different reactivity of metal species to various complexing agents gives the analyst an opportunity to determine which species are available. It is not possible to perform simultaneous multielement determinations or qualitative analyses. Finally, it is often necessary to concentrate the sample to a solid before redissolution, complexization and measurement, which increases the possibility of an error being introduced. The reader interested in more detailed information regarding UV-vis spectrometry is referred to Refs. 8 and 9.

Anodic Stripping Voltammetry

Anodic stripping voltammetry (ASV) is an electrochemical technique

that can be used for monitoring trace and ultratrace quantities of metals in water. Although its sensitivity is generally somewhat greater than that of AAS, the range of metals which can be detected is more limited. Only the metals listed in Table 5 (Ref. 10) are normally detected using ASV (or its counterpart, cathodic stripping voltammetry). It is most commonly used for four metals: copper, cadmium, lead and zinc.

ASV requires the plating out (reduction) of a metal in solution onto an electrode, and the subsequent reoxidation of that metal. The metal that is plated out depends upon the potential being applied and its amount on the current. The amount of metal deposited on the electrode is strongly dependent on the plating time and stirring rate, which must be reproducible. After the metal has plated out, the polarity of the electrodes is reversed. The potential is then gradually increased (a potential ramp) and the current measured. The metal will be reduced at its half-wave potential, the point of inflection in the current-voltage curve. The current recorded at the half-wave potential is a function of the amount of metal which has been plated out.

Although this technique is an old one, it is still changing with advances in technology. A variety of new electrodes are being used: hanging mercury drop electrodes (HMDE), a variety of mercury thin film electrodes (TFE), such as wax impregnated graphite electrodes, (WIGE), glassy carbon electrodes (GCE), rotating electrodes, and tubular electrodes. The thin film electrodes use a variety of substrates to support a film which provides a larger surface area for plating. The electrode area itself must be absolutely reproducible, and maintain its surface during analyses, since changing surface characteristics can

Table 5. Metals which may be determined using ASV and minimum detection limits for those metals

Metals[a]	mdl[d] (μg/ℓ)	Metal	mdl[d] (μg/ℓ)	Metal	mdl[d] (μg/ℓ)
Arsenic	<10[b]	Lead	0.01[c]	Silver	—
Antimony	—	Manganese	—	Thallium	2.0[c]
Barium	—	Mercury	—	Tin	0.01[c]
Cadmium	0.005[c]	Nickel	—	Zinc	0.04[c]
Cobalt	—	Platinum	—		
Copper	0.005[c]	Potassium	—		
Gold	—	Rhodium	10.0[c]		

[a]List of metals from Reference 10.
[b]Reference 11.
[c]Reference 12.
[d]Minimum detection limit

introduces errors into the results.

A variety of voltage potential waveforms can be used. Although some researchers still use a linear sweep, most report using a variety of squarewaves or pulsed techniques. The data is often displayed as rate of change of the current with time or potential since this enhances the signal and the sensitivity of the technique.[12]

Anodic stripping voltammetry is an extremely sensitive technique. The detection limits reported for a variety of metals are listed in Table 5. It is clear that sensitivity is one of the major advantages of this method. Furthermore, ASV can be used to determine ultratrace quantities of metals in brines without interferences from high concentrations of Ca^{+2} and Na^{+} ions. The technique can be used for qualitative and quantitative analyses and can be used to determine a limited number, usually four, metals simultaneously. It is even possible to tell something about the form of the metal while it is in solution by performing only minimal pretreatment.

The greatest disadvantages of this technique are the lack of standard procedures, the limited number of metals which can be analyzed, the problem of a sequestered metal being undetected, and the high degree of skill which is required of the operator. The reader interested in further literature is referred to the articles by Barendrecht,[13] and Copeland and Skogerboe.[12]

X-Ray Fluorescence Spectroscopy

X-ray fluorescence is a technique more commonly applied to solid samples than to aqueous ones. For those interested in monitoring water quality as revealed in sediments and biological specimens, it can be an

extremely useful technique. The principles behind x-ray fluorescence spectroscopy or x-ray emission spectroscopy are simple and similar to those for AES. The sample is bombarded with high energy photons or particles which excite the inner electronic levels of the analyte metal atom. A certain fraction of the excited atoms decay with the emission of x-rays whose wavelength is characteristic of the elements present. Its intensity is a function of the concentration of the metal in the sample. Other decay processes are possible, such as auger electrons emission:

$M^* \rightarrow M$ + auger electrons or x-ray emission.

The process for decay for most metals is known and is a statistical distribution usually between auger and x-ray emission. For metals with low atomic numbers the auger process is preferred; the x-ray process is preferred for heavier metals.

A number of variations of this technique are currently used; each optimizes the procedure to suit a different situation. There are two common sources of energy for activation: photons and charged particles. Also, two common methods for analyzing the emitted x-ray spectrum are used: energy-dispersive and wavelength-dispersive analysis. References 14 and 15 provide an introduction to the subject.

In energy-dispersive analysis, the spectrum emitted by the sample is allowed to impinge on a semiconductor detector. The associated circuitry then discriminates between the energies of the photons hitting it and counts the number in each energy range. An energy-dispersive spectrometer is shown in Figure 3a. In a wavelength-dispersive XRF spectrometer, the spectrum emitted by the sample is collimated and

directed onto a crystal which diffracts the x-rays and is used to direct successive wavelengths of radiation onto a detector (Figure 3b).

The advantages to energy-dispersive XRF are its ability to make simultaneous multielement determinations and the general simplicity of the mechanical design. On the other hand, the electronics involved are quite complex and the resolution achieveable is only ~ 150 keV, which is satisfactory to resolve the frequencies emitted by many high Z elements, although it is sometimes necessary to use a computer to deconvolute the spectra if elements of lower Z are involved.

Wavelength-dispersive analysis can be used for multielement simultaneous determination only when a complex multicrystal spectrometer is used. However, for routine determination of a single element repetitively, it is extremely valuable. Furthermore, the resolution observed is less than 10 keV which makes it possible to determine the oxidation state of the element present (for example S^{+6} from S^{+2}) and deconvolution of the spectrum is rarely necessary for analyses of the total metal.[17] A disadvantage is that even a single crystal instrument is mechanically complex, although the electronics involved are simple.

The techniques are particularly useful for trace analysis in solid samples or samples collected on filters such as sedimental or biological specimens, and suspended solids, since little or no sample preparation is necessary. (The values reported in Table 6 are actually results for a variety of air samples.) The technique is easily automated.

However, for aqueous samples, extensive preparation is necessary. Here the sample is usually taken to dryness or absorbed onto a variety of materials. By using these preconcentration techniques, extremely

Table 6. A comparison of minimum detection limits for various XRF techniques[a]

Metal	Wavelength Dispersion mdl (ng/cm^2)	Energy Dispersion	
		Photon induced mdl (ng/cm^2)	PIXE mdl (ng/cm^2)
Aluminum	1.3	160	—
Arsenic	6.0	1.6	0.5
Barium	0.8	25	—
Cadmium	1.2	3.6	14
Iron	12	5.3	0.13
Lead	32	4.5	2.5
Potassium	1.8	5.1	0.17
Selenium	12	1.3	0.6
Silica	3.4	62	—
Tin	1.4	4.7	—
Vanadium	2.4	11	0.09
Zinc	—	3.3	0.25

[a]Reference 14.

low detection limits can be achieved (see Table 7); however, preconcentration can be time consuming, tedious and may introduce errors.

All these methods of using XRF are accurate and precise. Detection limits obtainable for all these are compared in Table 6. The most serious disadvantage in using XRF is the expense involved. A minimal energy dispersive instrument begins at ~ $40,000 and wavelength dispersive spectrometers start at ~ $41,000. Further, because it is necessary to make careful preparations involving a high degree of skill, it is necessary to have a highly trained person to run, as well as to maintain and repair, the instrument and the analyses.

The interested reader is directed to Refs. 15 and 20 for an introduction to the entire field, Ref. 21 for wavelength dispersion, Ref. 16 for energy dispersion and Ref. 22 for an introduction to PIXE.

Neutron Activation Analysis

Neutron activation analysis (NAA) relies on bombardment of the sample by neutrons to induce radioactivity. The photon energy and intensity of the induced radiation is then measured, usually by a gamma ray spectrometer.

The technique is sensitive, accurate and precise. The reproducibility of the technique can be seen from Table 8. Metals present in ppb levels in a solid sample can be determined to a precision of less than 5% standard deviation even when two different laboratories analyze the same samples but with different procedures.[23] Neutron activation analysis cannot be used for speciation since the technique looks at nuclei; it is an excellent technique for simultaneous multielement determinations.

0 0 0 0 4 9 0 1 8 8 2

Table 7. Detection limits reported for determination of a variety of metals in aqueous samples after preconcentration on ion-exchange resin[a]

Metal	mdl (ppb)
Calcium	17.5
Chromium	0.8-3
Cobalt	0.4-3
Copper	0.4-3
Iron	1.5-3
Lead	< 5[b]
Manganese	0.8
Nickel	0.4
Potassium	14.4
Titanium	10.2
Vanadium	0.8
Zinc	0.6-3

[a]Data from Reference 18 (except that for lead).
[b]Datum for lead from Reference 19.

Table 8. A comparison of values for iron in a variety of samples, as determined by two separate groups using neutron activation analysis

Sample #	LBL Values (ppm)	Hebrew University Values (ppm)
1	5.44 ± 0.07	5.35 ± 0.06
2	5.15 ± 0.07	5.15 ± 0.06
3	7.17 ± 0.07	7.04 ± 0.08
4	0.547± 0.007	0.567±0.008
5	0.824± 0.008	0.845±0.011
6	0.594± 0.007	0.629±0.008

[a]Data presented in Reference 23.

The main disadvantage to the technique for use in determining metals in water is the need for preconcentrating the sample which is tedious and time-consuming and can introduce significant errors. Further, after the dry material is obtained, its preparation must be performed with meticulous care. A second disadvantage is cost--since most routine monitoring labs do not have a fission reactor at their disposal for activation. Third, for most procedures, it is not possible to get results in less than two weeks, since counting is usually done immediately after a low neutron flux density, but then a second count is made about two weeks after a second, higher flux density activation. And lastly, highly skilled personnel are necessary to run and maintain the equipment.

Water Quality Criteria

While the techniques and instruments for determination of metals in water have good sensitivity, water quality criteria for metals in water are often extremely stringent. Table 9 gives water criteria for several metals in waters used for a variety of purposes. Two types of criteria are given. First are the maximum contaminant levels allowed in drinking water by the Federal Safe Drinking Water Act (P.L. 93-523). Second are the minimum water quality criteria recommended by the EPA for waters used for a variety of purposes.[24,25] In its recommendation, the EPA sets limits as appropriate for each metal in water used for a specific purpose (e.g., domestic consumption, irrigation, freshwater aquatic life, etc.). Table 9 includes the lowest recommended criterion for each metal. Sometimes the criterion is relative; for example, it may read 0.01 times the 96 hour lethal concentration for 50% of the most sensitive species of the fish present in a particular body of water (96 hr. LC50). In this

Table 9. Water quality criteria

Metal	Max. contam. level safe drinking water act (μg/ℓ)[a]	Lowest Recommended Water Quality Criterion[b]		
		Level (absolute)	Level (relative)[c]	For protection of (example)
Arsenic	50	50	—	Domestic Water Supply-health
Barium	1000	1000	—	Domestic Water Supply-health
Beryllium	—	11	—	Freshwater Aquatic Life-soft water
Boron	—	750	—	Irrigation-Long Term, sensitive species
Cadmium	10	0.4	—	Freshwater Aquatic Life-Salmonids Cladocerans, soft water
Chromium	50	50	—	Domestic Water Supply-health
Copper	—	—	0.1×96 hr LC50 (2-3 μg/ℓ)	Freshwater and Maine Aquatic Life-(Rainbow Trout, Chinook Salmon)
Iron	—	300	—	Domestic Water Supply-Welfare
Lead	50	—	0.01×96 hr LC50 (1-5 μg/ℓ)	Freshwater Resident Species (Sticklebacks, Coho Salmon)
Manganese	—	50	—	Domestic Water Supply-Welfare
Mercury	2	0.05	—	Freshwater and Marine Aquatic Life-to protect human consumers

(continued)

Table 9. (continued)

Metal	Max.contam.level safe drinking water act (μg/ℓ)[a]	Lowest Recommended Water Quality Criterion[b]		
		Level (absolute)	Level (relative)[c]	For protection of (example)
Nickel	–	–	0.01×96 hr LC50 < 31[d] μg/ℓ	Freshwater and Marine Aquatic Life- (Marine Clam larvae)[d]
Selenium	10	10	–	Domestic Water Supply- health
Silver	50	–	0.01×96 hr LC50 < 0.06[d] μg/ℓ	Freshwater and Marine Aquatic Life- (oyster larvae)[d]
Vanadium	–	100[e]		Livestock Drinking Water
Zinc	–	–	0.01×96 hr LC50 1 μg/ℓ	Freshwater Aquatic Life- (Rainbow Trout)

[a]Safe Drinking Water Act, PL.93-523

[b]U.S. Environmental Protection Agency, Quality Criteria for Water (July, 1976).

[c]Often the criterion is expressed in relative terms, such as 0.01 times the 96 hour lethal concentration for 50% of the fish present (written 96 hr LC_{50} or LC50) based on a sensitive species. In these cases, examples of sensitive species are given and the criteria calculated based on the 96 hr LC50.

[d]In these two cases only 48 hr LC50's were given for the sensitive species.

[e]From NAS,NAE, Water Quality Criteria, 1972 (1974).

case, the table includes the relative criterion (e.g., 0.01 x 96 hr. LC50) and a specific example of the absolute criterion which might be derived. For example, for copper, the 96 hour LC50 for rainbow trout is 0.020 mg/l; the criterion is 0.1 x the 96 hr LC50 and therefore the derived absolute criterion is 2 μg of Cu/l, if the body of water contains rainbow trout.

Trace levels have been recommended for all the metals listed. Many (e.g., arsenic, cadmium, lead, mercury, chromium) are known to be toxic to man. Others (e.g., boron, vanadium), while relatively harmless to man, may be more harmful to other forms of life.

For arsenic, barium, chromium and selenium, the primary drinking water standards and the most stringent water quality criteria are the same, (50, 1000, 50 and 10 ppb respectively) for cadmium and mercury; the criteria for freshwater aquatic life of 0.4 and 0.05 ppb (μg/l) are substantially less than the primary drinking water standards (10 and 2 ppb). Often the relative criteria result in absolute values which are substantially less than those for the same metal in drinking water (see copper, lead, and silver). It is interesting to realize that often the most sensitive species being protected are common food species, trout, salmon, oysters or clams. Trace metals are not only toxic to young trout and salmon, they can seriously influence breeding and spawning characteristics of the adult fish. Trace metals can be harmful to oysters and clams, but these metals can also be concentrated by them until the shellfish themselves become toxic or harmful to man.

Instrumental Detection Limits vs. Water Quality Criteria

Because of the proven toxicity or detrimental nature of many metals

when in the aqueous environment, it is important to determine their presence accurately and precisely.

As a preliminary procedure, to determine the effectiveness and scope of the above techniques in determining metals in water at the concentrations recommended, a comparison has been made of the minimum detectable limit, mdl, reported for each technique that is found in the technical and reviewed literature. The mdl was chosen since it is a figure often quoted as providing a rough measure of the sensitivity of a variety of instruments and techniques.

Table 10 compared the lowest water quality criterion for a series of five metals: arsenic, cadmium, chromium, lead and mercury, with the mdls reported for AAS both flame and flameless, for ICP-AES, for XRF and for anodic stripping voltammetry. These metals were chosen because they are all currently considered toxics. Mercury, lead and cadmium have already been associated with incidents of illness, disability and death due to water contamination. Arsenic poisoning is well-known and chromium(VI) has recently come under suspicion as a possible carcinogen.[24]

The mdls are reported in a common unit, ppb or µg/l. For AAS, flame and AES-ICP, this is usually the value reported by the manufacturer. For flameless AAS, a volume must be specified since the mdl is often given as an absolute value, usually in 10^{-12}g, and is highly dependent on the sample size. The size sample chosen was 10 µl, even though the size sample specified by the manufacturers is usually 100 µl. Since graphite furnaces can rarely handle a sample larger than 50 µl and 10-20 µl is a more normal sample, 10 µl seemed more appropriate.

Samples for XRF require preconcentration; therefore the mdl is

Table 10. Minimum detection limits reported in the technical and reviewed literature compared to water quality criteria

Metal	Lowest Recommended Water Quality Criterion (μg/ℓ)[a]	AAS Flame[b] (μg/ℓ)	Flameless[c] (μg/ℓ)	AES-ICP[d] (μg/ℓ)	XRF ppb	ASV (μg/ℓ)
Arsenic	50 (Domestic Water Supplies)	0.1-1	0.6-7.5	20-330	—	<10[g]
Cadmium	0.4 (Soft, Freshwater Salmonids and Cladocerans)	0.15-2	0.01-0.04	1-5	—	0.005[h]
Chromium	50 (Domestic Water Supplies)	3-8	0.05-0.1	2-6	0.8-3[e]	—
Lead	1 (Coho Salmon - 0.01 × 96 hr LC50)	10-30	0.15-5	20-50	< 5[f]	0.01[h]
Mercury	0.05 (Freshwater Aquatic Life and Wildlife)	0.1-0.5	6	0.4-3	—	—

[a]See Table 8 for references.

[b]Jarrell-Ash, Instrumentation Lab., Perkin Elmer, Varian, manufacturers specifications, 1977.

[c]Based on a 10 μℓ sample, Jarrell-Ash, Instrumentation Labs., Perkin Elmer, Varian, manufacturers' specifications.

[d]Applied Research Labs., Jarrell Ash and Labtest Equipment, manufacturers' specifications, 1977.

[e]Reference 17.

[f]Reference 18.

[g]Reference 11.

[h]Reference 12.

highly dependent upon the size sample that the analyst has and is willing to preconcentrate. The values for ASV are also relative since preconcentration is involved.

Table 10 raises many questions regarding the adequacy of current instrumental procedures to produce meaningful data at the levels specified by the criteria. For example, flame AAS is the most commonly used technique for determining all five metals--and yet the minimum detection limits reported by the manufacturers for flame AAS for these five metals are actually higher than the criteria for cadmium, lead and mercury.

If one examines the detection limits reported for all the techniques for mercury, none are lower than the criterion for fish and wildlife (0.05 ppb). For the other metals, the manufacturers report that flameless AAS has a lower detection limit than the criteria, although for lead, the mdl is only of the same order of magnitude. For arsenic and chromium, all three techniques have mdls reported which are lower than the criteria.

Nevertheless, it is clear from comparing the mdl with the criteria that it would be difficult to obtain meaningful results using these techniques without some prior concentration. It is important to remember when considering mdls that these are often reported using samples analyzed under optimal conditions, not the environmental samples which must be analyzed and may be heavy with sewage, sediment or algae, or have a high salinity or merely interfering ions. Nor do mdls take into consideration the errors which could be introduced in sampling, transport, chemical pretreatments or preconcentration. The EPA ran quality assurance tests and the percentage standard deviations for the standard methods

for these metals near the Safe Drinking Water criteria were: As, ±5%; Cd, 78%; Cr, 39%, Pb, 48%; and Hg, 43%.

Clearly, a comparison of detection limits is only a first step in considering the technique which is to be used and in evaluating a monitoring strategy. Other factors considered for each instrumental technique are the range of metals which can be monitored using a single technique or instrument, and the capacity of the instrument for making simultaneous multielement determinations and qualitative analyses. Further, one must consider the time and expertise required in making single and multiple repetitive determinations and the expense of the instrument in terms of time, personnel and cost.

For example, AAS both flame and flameless, AES, XRF and Neutron Activation Analysis can be used to monitor most metals (although there are a few glaring exceptions--for example, NAA is very insensitive to lead). Anodic stripping is not used for as many metals, but is very sensitive to Cr, Cd, Cu and Zn, and it can be used to analyze for these metals simultaneously at ppb and trillion levels. Furthermore, the measurement is unaffected by saline water. On the other hand, AAS and UV-vis spectrometry are not appropriate techniques for performing simultaneous determinations or qualitative analyses. However, for making a single analysis or repetitive quantitative analyses, they are generally less costly, and require less time and training to perform routine analyses than do some of the other techniques. XRF and NAA are used for both simultaneous determinations and qualitative analyses, but require expensive equipment, complicated sample preparation, and highly skilled personnel to maintain the equipment.

It is also necessary, of course, to consider the scope of the monitoring program as a whole, its purpose and goals. One must consider the entire group of pollutants to be determined, the set of metals to be monitored, the number of measurements to be performed and how often they must be repeated.

Most monitoring programs, currently active, involve monitoring for a specific set of metals, as is required by most regulatory agencies. Two important factors are often ignored: speciation and qualitative analyses for unsuspected pollutants. Rarely is speciation required, yet it is clear that methyl-mercury is far more toxic than is inorganic mercury, and Cr(VI) is a suspected carcinogen, whereas Cr(III) is still believed to be relatively harmless.

Qualitative analysis is rarely required, yet it might reveal the presence of unsuspected metals which are themselves dangerous. It could establish the presence of metal ions or forms which have an antagonistic or synergistic effect with the known ions, thereby changing the interpretation of the data concerning the effect of the known ion on the measurement or the environment.

Summary

As a result of the survey, it is clear that several issues must be explored in greater detail. First, one must consider the value of measurements made, when under the best conditions the detection limit of the instrument used is of the same order of magnitude as the quantity of metal to be measured and when standard deviations run around 30-50%. Secondly, one must establish a balance between the sensitivity required of the instrument which is used and the skill of the operator required

to perform accurate and precise analyses. And finally, one must consider the effectiveness of metal monitoring programs which emphasize quantitative determination of pollutants known or suspected to be present, but place low priority on routine qualitative analyses to establish which pollutants are actually there.

This work was supported by the Division of Biological and Environmental Research of the Department of Energy.

REFERENCES

1. Environmental Instrumentation Survey Group, "Survey of Instrumentation for Environmental Monitoring," Lawrence Berkeley Laboratory Report, LBL-1, 1971-76, continuing project.

2. G.F. Kirkbright and M. Sargent, Atomic Absorption and Fluorescence Spectroscopy, Academic Press, London, 1974.

3. Code of Federal Regulations, Title 40, part 136. (abbreviated 40 CFR 136).

4. American Public Health Association, American Water Works Association, Water Pollution Control Federation, Standard Methods for the Examination of Water and Wastewater, 14th ed., 1976. American Public Health Assoc., 1015 Eighteenth St. N.W. Washington, D.C. 20036.

5. U.S. Environmental Protection Agency, Methods for Chemical Analysis of Water and Wastes, Methods Development and Quality Assurance Laboratory, National Environmental Research Center, Cincinnati, OH, 45268, 1974. EPA Doc. # EPA 625/6-74-003.

6. H.H. Willard, L.L. Merritt, Jr. and J.A. Dean, Instrumental Methods of Analysis, 5th ed. D. Van Nostrand, New York, 1974.

7. C. Veillon, "Optical Atomic Spectroscopic Techniques," in Trace Analysis, Spectroscopic Methods for Elements, J.D. Winefordner ed., J. Wiley & Sons, New York, 1976, pp. 123-181.

8. P.A. St. John, "Optical Molecular Spectroscopic Methods," in Trace Analysis, Spectroscopic Methods for Elements, J.D. Windfordner ed., J. Wiley & Sons, New York, 1976, pp. 183-212.

9. E.B. Sandell, Colorimetric Determination of Trace Metals, Interscience, New York, 1959.

10. F.P.J. Cahill and G.W. Van Loon, "Trace Analysis by Atomic Absorption Spectroscopy and Anodic Stripping Voltammetry," American Laboratory, August 1976, p. 11.

11. P.H. Davis, et al, "The Analysis of Arsenic and Lead in Imported Wine by Anodic Stripping Voltammetry," Abstracts of the 1977 Pittsburg Conference on Analytical Chemistry and Applied Spectroscopy, February 28 - March 4, 1977, Cleveland, OH, paper #263.

12. T.R. Copeland and R.K. Skogerboe, Anal. Chem., 46, 1257A (1974).

13. E. Barendrecht, "Stripping Voltammetry," in Electroanalytical Chemistry, Vol. 2, A.J. Bard ed., Marcel Dekker, Inc., New York, 1967.

14. J.M. Jaklevic and R.L. Walter, "Comparison of Minimum Detectable Limits Among X-Ray Spectrometers," in X-Ray Fluorescence Analysis of Environmental Samples, T.G. Dzubay, ed. Ann Arbor Science, Ann Arbor, 1977, pp. 63-75.

15. R.V. Slates, "X-Ray Fluorescence Spectrometers: A Comparison of Wavelength and Energy Dispersive Instruments," E.I. DuPont de Nemours, Savannah River Laboratory, Aiken So. Carolina, 25801, November 1977.

16. J.M. Jaklevic and F.S. Goulding, "Energy Dispersion," Lawrence Berkeley Laboratory Report No. LBL-5354, May 1976. To be published in a Chapter in Practical X-Ray Spectroscopy, L.S. Birks, ed., Marcel Dekker.

17. L.S. Birks, "Wavelength Dispersion," in X-Ray Fluorescence Analysis of Environmental Samples, T.G. Dzubay, ed., Ann Arbor Science, Ann Arbor, 1977.

18. R.E. Van Grieken, C.M. Bresseleers, B.M. Vander Borght, Anal. Chem., 49, 1326 (1977).

19. D.T. Carlton, and J.C. Russ, XRS, 5, 172 (1976).

20. D.E. Leyden, "X-Ray Emission Spectrometry and Environmental Water Analysis," American Lab, November, 1974 p. 24.

21. L.S. Birks, X-Ray Spectrochemical Analysis, 2nd ed. Interscience, New York, 1969.

22. "Proceedings of the International Conference on Particle Induced X-Ray Emission and Its Analytical Applications," Lund Sweden, August 23-26, 1976, ed. S.A.E. Johannsson, Nucl. Inst. and Methods, 142, 1977.

23. J. Yellin, I. Perlman, F. Asaro, H. V. Michel, and D. F. Mosier, "Comparison of Neutron Activation Analysis from the Lawrence Berkeley Laboratory and The Hebrew University", Lawrence Berkeley Laboratory Report No. LBL-5298.

24. U.S. Environmental Protection Agency, "Quality Criteria for Water," Washington, D.C. 20460, July 1976.

25. NAS/NAE, Water Quality Criteria, 1972 (1974).

0 0 0 0 4 9 0 1 8 8 8

FIGURE CAPTIONS

Figure 1. Simplified schematic diagram of an atomic absorption spectrometer.

Figure 2. Simplified schematic diagrams of atomic emission spectrometers.

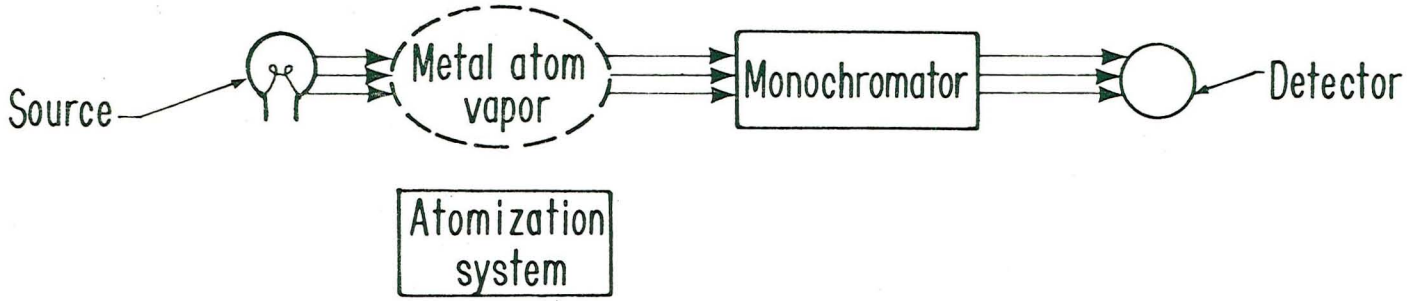
a. Spectrum analysis using a monochromator.

b. Spectrum analysis using a polychromator.

Figure 3. X-ray fluorescence spectrometry.

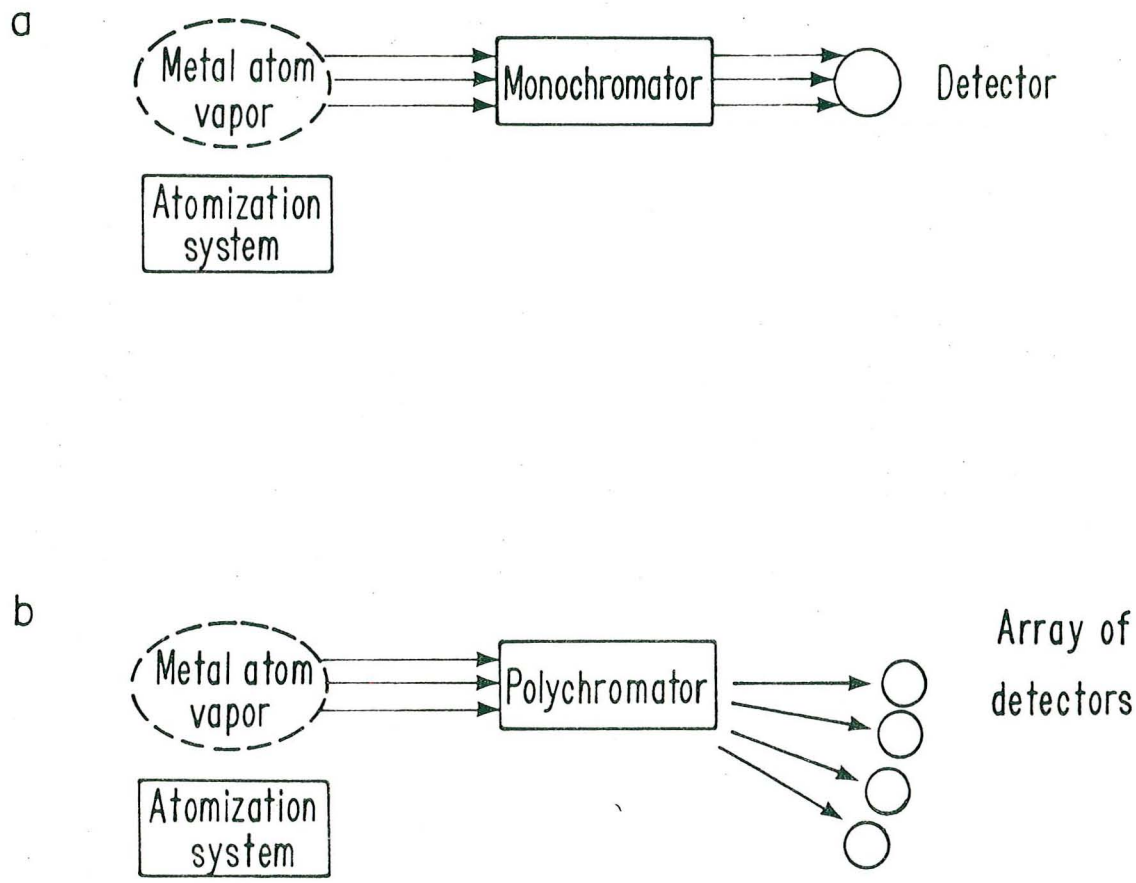
a. Simplified schematic diagram illustrating an energy-dispersive spectrometer (Ref. 16).

b. Simplified schematic diagram illustrating a wavelength-dispersive spectrometer (adapted from Ref. 6).



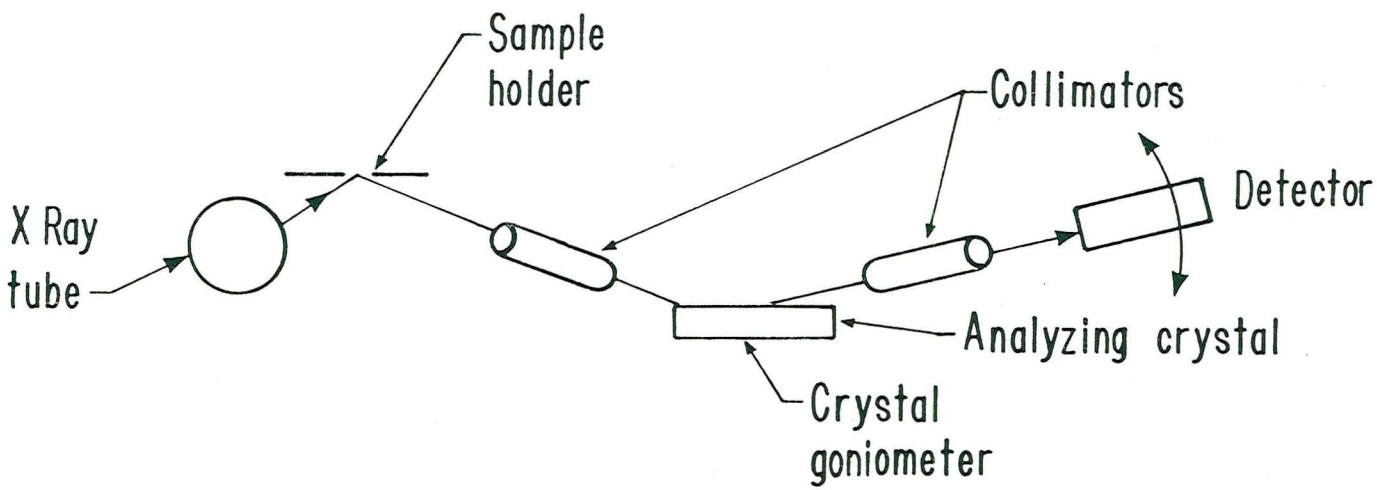
XBL 787-2603

Fig. 1



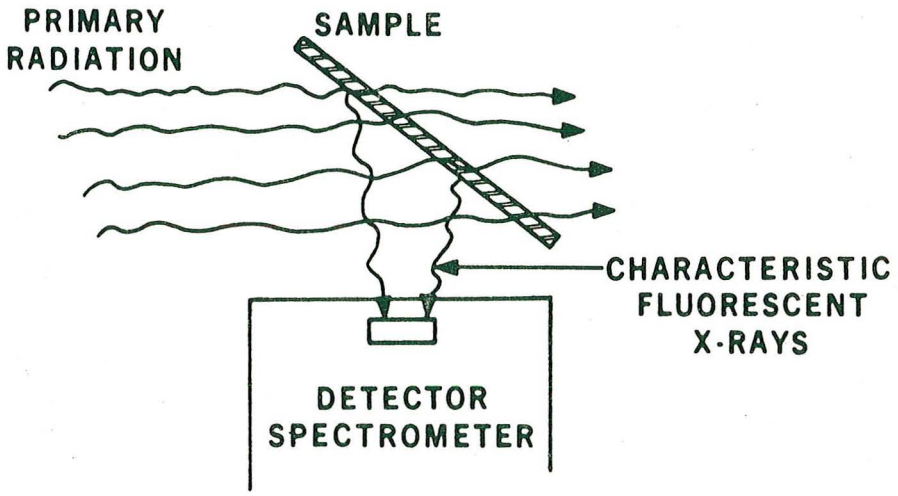
XBL 787-2604

Fig. 2



XBL 787-2602

Fig. 3 a.



XBL 733-287A

Fig. 3 b

This report was done with support from the United States Energy Research and Development Administration. Any conclusions or opinions expressed in this report represent solely those of the author(s) and not necessarily those of The Regents of the University of California, the Lawrence Berkeley Laboratory or the United States Energy Research and Development Administration.

0 0 0 0 4 5 0 2 2 9 4