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Manual of Analytical Methods for the Industrial Hygiene Chemistry Laboratory

K. A. Greulich, C. E. Gray

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MANUAL OF ANALYTICAL METHODS FOR THE INDUSTRIAL HYGIENE CHEMISTRY LABORATORY

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FORWARD

This Manual is compiled from techniques used in the Industrial Hygiene Chemistry Laboratory of Sandia National Laboratories in Albuquerque, New Mexico. It is a revision of three earlier publications, SC-M-67-3044, edited by L. W. Brewer; SAND75-0014, edited by C. E. Gray; and SAND88-1149, edited by K. A. Greulich, C. E. Gray, and B. M. Kelly.

The procedures are similar to those used in other laboratories devoted to industrial hygiene practices. Some of the methods are standard; some, modified to suit our needs; and still others, developed at Sandia. The authors have attempted to present all methods in a simple and concise manner but in sufficient detail to make them readily usable. It is not to be inferred that these methods are universal for any type of sample, but they have been found very reliable for the types of samples mentioned. The authors welcome inquiry for clarification of any part of this manual. We hope that the document will be of use and service to others.

The loose-leaf format is intended to permit the later inclusion of new and revised procedures as they become available.

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SECTION A

INTRODUCTION

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ENVIRONMENT, HEALTH, AND SAFETY CONCERNS

The Industrial Hygiene Chemistry Laboratory is operated in such a manner to insure the protection of both the environment and the laboratory staff. The guidelines are specified in the Corporate Chemical Hygiene Plan and in Activity-Specific ES&H Standard Operating Procedure (SOP) SP471521, Operation of the Industrial Hygiene Chemistry Laboratory (Date). The SOP indicates proper storage, handling, disposal of hazardous chemicals, including flammables, highly toxic materials, and carcinogens.

CONSULT THE APPROPRIATE MATERIAL SAFETY DATA SHEET BEFORE USING HAZARDOUS MATERIALS. Warnings for particular hazards are listed in the individual procedures. Hazard terms used in the ES&H NOTES include the following:

ACGIH - American Conference of Governmental & Industrial Hygienists

A1 - Confirmed human carcinogen

A2 - Suspected human carcinogen

IARC - International Agency for Research on Cancer

1 - Carcinogenic to humans

2A - Probably carcinogenic to humans

2B - Possibly carcinogenic to humans

NTP - National Toxicology Program.

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ANALYTICAL LABORATORY -- FIELD GROUP INTERFACE

POLICY

The purpose of sampling and analysis is to obtain valid data, describing a particular situation, which can be interpreted as a basis for possible action. Therefore the chemistry lab - field group interface must be carried out with a clear purpose and with an understanding of both the problem to be solved and the physical conditions that exist.

SAMPLING STRATEGY

1. Before taking any samples, especially using a new sampling procedure, contact the laboratory staff to assure that your samples will meet the requirements of the analytical technique. Among the topics that need to be discussed are the following:
  - a. Whether they can be run at all. If we do not currently have an appropriate technique, we may need time to develop and validate a new procedure and to acquire necessary standards.
  - b. Whether they can be run within the required holding time limit
  - c. The appropriate sampling techniques, containers, and quantities required (very important)
  - d. Apparatus and reagents needed for each analyte and matrix
  - e. Collection techniques and appropriate handling of samples to prevent contamination or loss of analyte
  - f. The prescribed preservation techniques.
  - g. Interferences with the analytical method
  - h. Range and sensitivity of the analytical method.
2. When untrained people are allowed to take samples, the value of the data comes into question unless we can be sure the samples were properly taken, prepared, stored, and recorded.
3. Place sealing tape around the joints of air filter cassettes to prevent leaks.
4. SKC recommends that the openings of a charcoal tube be about one-half the tube diameter.

5. Include at least one blank when submitting air filters, swipes, charcoal badges, or sorption tubes. The blanks need not be assigned a field log number. They may simply be placed in a container (paper or plastic envelope, etc.) and labeled "Blank."
6. When requesting analysis of a mixture (such as Stoddard solvent, naphthas, cleaning compounds, etc.), submit a bulk sample to permit location and standardization of peaks.
7. For sample submitters who have other regular sample providers, assure that they understand the rules for sample submission and that they have a supply of labels, seals, and forms. Someone must assign an appropriate identification number and maintain the field records.
8. Samples that cannot be analyzed in our laboratory may be sent out to a contract analytical lab. If we need analyses for materials other than those currently assigned, a new contract will have to be placed; so leave plenty of time. All samples sent to contract labs must go through the Industrial Hygiene Lab, where they will be assigned a lab log number, be logged into the sample data system, and be accompanied by completed chain-of-custody and laboratory request forms for the appropriate contract lab.

CHAIN-OF-CUSTODY PROCEDURES FOR SAMPLES SUBMITTED TO THE INDUSTRIAL HYGIENE CHEMISTRY LABORATORY

INTRODUCTION

Good analytical practices, as well as potential legal problems, suggest the need for ensuring the integrity of industrial hygiene and environmental samples collected for Sandia National Laboratories, Albuquerque, and analyzed in the Industrial Hygiene Chemistry Laboratory. "Chain-of-custody" procedures allow one to trace the possession and handling of samples from the time of collection through analysis and final disposition.

Three important components of any chain-of-custody program are: 1) sample seals/labels, 2) chain-of-custody records, and 3) sample analysis request sheets. Samples may be considered secure if they are: 1) in the physical possession of an individual, 2) locked in an area of limited access, or 3) closed with a seal which must be broken when the container is opened.

The procedures discussed below will be followed for all samples submitted for analysis to the Industrial Hygiene Chemistry Laboratory. The forms and recommendations are based on those described in Reference 1.

SAMPLE SEALS/LABELS

All samples submitted to the Industrial Hygiene Laboratory must be sealed and labeled. The label may serve as the seal, if appropriately applied. Each label should contain, at a minimum, the following information:

Sample number/identification

Name and organization of the collector

Date of collection

Place of collection.

Figure A-1 is a copy of the labels available from the Laboratory. Others are acceptable as long as they contain the necessary information.

The seals/labels should be placed on the sample container at the time of collection. The information included on the label should also be recorded in a field log book, along with any other pertinent data required by the collector. Sample numbers should be unique and may include the collector's initials plus a

ENVIRONMENTAL HEALTH SAMPLE

Sample No.: _____

Collector: _____ Org.: _____

Date: _____

Location: _____

FIGURE A-1. LABEL FOR INDUSTRIAL HYGIENE SAMPLES

number that will not be repeated within the foreseeable future. (That is, do not label two series of samples xxx1, xxx2, xxx3, etc.; rather, make the numbers for the two series continuous.) Alternatively, continuous field log numbers may be used. Do not repeat field log numbers the next year.

CHAIN-OF-CUSTODY RECORDS

Sample possession must be traceable from the time of collection to the time of disposal. Traceability will be ensured by a Chain-of-Custody record which must accompany every sample submitted to the Lab for analysis. As illustrated in Figure A-2, a Chain-of-Custody form is included with the Laboratory Services form. If, in addition, the submitting organization has its own chain-of-custody document, this form should also be supplied with the sample. As indicated in the Figure, the following information must be included:

Field log number/sample description

Signatures of all people involved in the chain of possession, including the collector, deliverer, and chemist. If the person submitting the sample did not collect it, the collector's signature **must** be on the sheet.

Inclusive dates of possession

Final disposition of the sample.

Because the form must be signed upon receipt of the sample, samples must be given to one of the laboratory staff, not merely left in the sample prep room. If the Laboratory chemists are gone, the collector must retain possession of the samples. The original Chain-of-Custody form will be maintained in the analytical lab files, and a copy will be returned to the sample supplier for inclusion in his/her files.

REQUEST FOR ANALYSIS

When submitting samples to the Industrial Hygiene Laboratory for analysis, the sample supplier must complete a Laboratory Services form (see Figure A-2). The form includes the following information:

Name and organization of the sample supplier

Date sample was submitted

Reference employee and organization

Laboratory Services/Chain of Custody Form

Page _____ of _____

Relinquished By _____	Date/Time _____	Received By _____	Date/Time _____
Relinquished By _____	Date/Time _____	Received By _____	Date/Time _____
Relinquished By _____	Date/Time _____	Received By _____	Date/Time _____
Issued to/for Transfer _____		Disposal By _____	Date/Time _____
Approved By _____	Chem Lab _____	Supervisor _____	Date _____

A-10

Location sample was taken

Contaminant to be analyzed

Laboratory log number.

In addition, for air samples always include the sampling time and rate or the total volume sampled. This information can help us decide what technique to use for the analysis. Some description, even a brief one, should be included with the Field ID number. Important information includes the person who was monitored (air samples), the approximate area sampled (swipes), and other elements or compounds coexisting with the desired analyte in your sample (because these may cause interferences with the analytical technique).

Samples, with the completed Laboratory Services/Chain-of-Custody forms, will be given to one of the analytical chemists, who will inspect the sample seals and reject any sample having a breached seal, or no seal. He will also assign unique laboratory log numbers to each sample to assure that samples and analytical results are properly correlated. A separate number will be assigned for each individual analysis requested for a given sample. For that reason, only one analyte per form is permitted.

Complete the "Reference" portion of the Laboratory Services form with the name of an employee in the area sampled and the location where the sample was taken (not the office of the referenced employee or sample supplier). This will facilitate data searches on the records computer.

Disposal instructions may be included by the sample supplier. If no instructions are provided, the chemist will note the final disposition of the sample on the form.

REFERENCES

1. Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, Publication No. SW-846 (3rd ed; Washington, DC: U.S. Environmental Protection Agency, 1986).

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QUALITY CONTROL

INTRODUCTION

Because of the importance of laboratory analyses and the resulting actions which they produce, a program to insure the reliability of the data is essential. All analysts practice quality control to varying degrees, depending upon their training, professional pride, and awareness of the importance of the work they are doing. However, under the pressure of daily workload, analytical quality control may be inadvertently neglected. Therefore an established routine control program, applied to every analytical test, is important in assuring the quality of the final results. The following program is designed to measure the Quality Control (QC) of the Industrial Hygiene Chemistry Laboratory.

RESPONSIBILITIES

1. Laboratory QC data will be maintained along with sample results.
2. Standards and a blank will be analyzed with every series of samples.
3. Spiked samples may be used whenever appropriate and sample size permits. When possible, a spiked blank filter will be analyzed. When running urine or water samples, an aliquot of every tenth sample may be spiked and analyzed with the sample series.
4. Each analyst will (a) routinely check, calibrate, and maintain equipment and instruments in good working order; (b) routinely check procedures and reagents; and (c) maintain good housekeeping practices, cleanliness of the work areas, and general orderliness.

CONTROL CHARTS

Control charts are compiled for each of the applicable determinations. These include:

1. Percent recoveries of all spiked and commercial control samples
2. Tritium blank in cpm and Efficiency of the tritium standard
3. Uranium standard of 0.01, 0.1, 1, and 10 PPM
4. Arsenic at 10 PPM absorbance for flame AA
5. Beryllium at 1 PPM absorbance for flame AA
6. Cadmium at 1 PPM absorbance for flame AA

7. Copper at 5 PPM absorbance for flame AA
8. Iron at 10 PPM absorbance for flame AA
9. Lead at 10 PPM absorbance for flame AA and 10 PPB peak height for graphite furnace
10. Lithium at 1 PPM absorbance for flame AA
11. Manganese at 5 PPM absorbance for flame AA
12. Nickel at 5 PPM absorbance for flame AA
13. Zinc at 1 PPM absorbance for flame AA
14. pH 7 buffer
15. Specific conductivity of 1413 $\mu\text{mho/cm}$ standard

LOG BOOKS

Permanent logbooks or records are kept to document the following procedures:

Preparation of calibration standards and reagents

Calibration of gravimetric and volumetric equipment

Repair and preventive maintenance of analytical instruments.

INTERLABORATORY REFERENCE SYSTEMS

The analytical laboratory participates in interlaboratory intercomparison studies whenever possible. The current programs are:

1. The AIHA/NIOSH Proficiency Analytical Testing (PAT) program
2. The EPA-sponsored Radioactive cross-check program, run occasionally in cooperation with Division 3213, Health Instrumentation
3. The DOE/EML-sponsored Radioactive environmental study, run occasionally in cooperation with Division 3213, Health Instrumentation.

SECTION B

INORGANIC METHODS

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COMMON ANIONS IN AQUEOUS SOLUTIONS

ABSTRACT

Ion chromatography is a low-pressure, high-performance, liquid-chromatographic technique for the determination of ions by separation on a low capacity ion exchange column. The sample is delivered by a stream of flowing eluent to the top of a separator column, where separation occurs based on the relative affinities of the ions for the functional group of the column packing. The separated ion bands then pass through a suppressor column having a functional group with a charge opposite to that of the separator packing. This column neutralizes the eluent ions to suppress their conductivity and enhances the conductivity of the analyte ions, thus improving the sensitivity.

Anions of strong acids can be detected easily using a conductivity detector. Retention times and detection limits for several common anions are listed in Table B-1.*

APPLICATIONS AND LIMITATIONS

Ion chromatography is a fairly rapid, highly sensitive technique, having a precision of 1-5% at low concentrations between 10 PPB and 100 PPM. Calibration is often linear over 4 orders of magnitude. The equipment is relatively inexpensive, and the technique usually requires little or no sample preparation for clean samples or even those containing large quantities of salts (brines, etc.).

The main disadvantages are as follows: (1) Because the conductivity detector responds to any anion, identification relies upon retention time. (2) Interferences sometimes limit the number of anions that can be analyzed in a single run. (3) Procedures often must be adjusted to achieve adequate separations. These disadvantages are common to all forms of chromatography.

APPARATUS

Ion chromatograph, Dionex Model 2110i with conductivity detector

Integrator, Hewlett-Packard Model 3390A or 3396A

Syringes, 5 cc, plastic

---

* Retention time is influenced by flow rate, pressure, and age of column. Times in Table B-1 are based on a flow rate of 138 ml/hr. See Reference 3.

REAGENTS

Eluent solution, 0.0029M NaHCO₃/0.0023M Na₂CO₃ - Dissolve 0.9744 ± 0.0005 g of NaHCO₃ and 0.9752 ± 0.0005 g of Na₂CO₃ in 4 liters of distilled water.

Regenerant solution, 0.025N H₂SO₄ - Dilute 2.8 ml of concentrated H₂SO₄ to 4 liters with distilled water.

ANALYTICAL PROCEDURE

1. Conditions:
  - a. Separator column: Dionex HPIC-AS4 anion exchange column, 3 x 500 mm
  - b. Suppressor column: Dionex AFS (anion fiber suppressor)
  - c. Flow settings: High pressure limit 1500 psi
Low pressure limit 0 psi
Flow rate 2 ml/min
2. Turn on the air to the pneumatic valves, the power to the chromatograph, the regenerant flow, and the eluent flow.
3. Press the START button, and watch the pressure rise. If the pressure rises to the maximum, the system is ready to run. If it stays low, the pump probably needs priming with ethanol (see Reference 4). If the back pressure rises high enough to shut down the system, replace the pre-filter.
4. When the READY light comes on, turn on CELL and AUTO OFFSET; and wait for the conductivity reading to stabilize. With AUTO OFFSET turned off, the reading should be ≤25 for this eluent. When AUTO OFFSET is on, it cancels out the baseline and should be stable at <0.1.
5. Draw about 5 ml of sample into a plastic syringe, and attach it to Sample Port 1. Inject about 1 ml of sample, excluding any bubbles, until liquid exits the tubing on the front of the instrument.
6. Set the integrator parameters to the values listed in the Integrator Quick Reference Guide (Reference 5).
7. Reset the AUTO OFFSET to zero; then push the SYS 1 INJECT Button and the integrator START Button simultaneously. The anion run requires about 20 minutes to complete.

8. Peaks are identified by their approximate retention times. For each peak, the integrator lists retention time, area, area-to-height ratio, and percent area. In addition, it draws a chromatogram of the run.
9. For quantitative results, run appropriate standards and prepare calibration graphs of peak area versus concentration.
10. After the last run, inject distilled water and run for 30 minutes to purge the exchange system before shutting down.

REFERENCES

1. J.S. Fritz, "Ion Chromatography," Anal Chem 59(4):335A (1987).
2. D.T.E. Hunt and A.L. Wilson, The Chemical Analysis of Water (2nd ed; London: The Royal Society of Chemistry, 1986), p. 489.
3. Ion Chromatography Training Course (Sunnyvale, CA: Dionex Corp., 1978).
4. Series 2000i Operations Manual (Sunnyvale, CA: Dionex Corp., 1978).
5. 3390A Reporting Integrator Quick Reference Guide, Publication No. 03390-90004 (Avondale, PA: Hewlett-Packard, 1980).

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TABLE B-1

ION CHROMATOGRAPHIC DATA FOR COMMON ANIONS

ANION	RETENTION TIME, min.	METHOD DETECTION LIMIT, mg/L
F ⁻	2	0.05
Acetate	2	0.1
Formate	3	0.1
Cl ⁻	3	0.07
NO ₂ ⁻	4	0.5
PO ₄ ⁻³	8	0.2
Br ⁻	9	0.5
NO ₃ ⁻	14	0.3
SO ₄ ⁻²	18	0.1
Oxalate	20	0.5

ARSENIC IN AIR, URINE, AND WATER

ABSTRACT

Ashed samples are reduced to trivalent arsenic, evolved as arsine gas, and collected in silver diethyldithiocarbamate which is then determined colorimetrically at 560 nm.

ES&H NOTES

Inorganic arsenic and many of its compounds are designated as NTP known human carcinogens and as Class 1 carcinogens by the IARC. They are also moderately to highly toxic. These materials should be handled in a Designated Area, typically a laboratory hood. The room and/or hood shall be clearly labeled with a sign indicating that a carcinogen is in use.

APPARATUS

Spectrophotometer, Hewlett-Packard Model 8450A or equivalent with 1-cm cells

Arsine generator (Figure B-1)

A = Generator flask

B = Scrubber with glass wool plug of lead acetate

C = Evolution tube

Figure B-1. Arsine Generator

REAGENTS

Nitric acid, conc. (70% HNO_3)

Perchloric acid, conc. (70% HClO_4)

Sulfuric acid, conc. (96% H_2SO_4)

Acid digestion mixture II, 3:1:1 conc. HNO_3 : conc. H_2SO_4 :
conc. HClO_4

Ammonium oxalate, saturated solution

Hydrochloric acid, conc. (36% HCl)

Silver diethyldithiocarbamate

Pyridine

Arsine absorbing solution - Dissolve 1 g of silver diethyldithiocarbamate in 200 ml of A.R. pyridine. Filter the solution before use. Store in a brown bottle.

Potassium iodide solution - Dissolve 15 g of KI in 100 ml of water. Store in a brown bottle.

Stannous chloride solution - Dissolve 40 g of stannous chloride dihydrate in 100 ml of conc. HCl.

Lead acetate solution - Dissolve 10 g of lead acetate in 100 ml of water. Glass wool in the scrubber is soaked in this solution, drained, and dried.

Zinc, granular 20 mesh

Arsenic standard solution (1 mg/ml) - Dissolve 0.660 g of As_2O_3 in 10 ml of 20% NaOH, then dilute to 500 ml. CAUTION: THIS SOLUTION IS TOXIC!

ANALYTICAL PROCEDURE

1. Transfer the filter paper sample or 25 ml of urine or 25 ml of water into a 150-ml beaker.
2. Ash the sample using 5-10 ml of digestion mixture II, and heat on a 140°C hot plate. Continue heating to white fumes of SO_3 .
3. Cool; add 10 ml of distilled water and 5 ml of a saturated solution of ammonium oxalate; and again heat to fumes of SO_3 to remove all traces of nitric acid.
4. Cool, add 10 ml of conc. HCl, and quantitatively transfer with distilled water to a 50-ml graduated cylinder.
5. Transfer a 25-ml aliquot to the generator flask.
6. To the evolution tube add 3 ml of the pyridine-silver diethyldithiocarbamate absorbing solution.
7. To the sample solution in the generator flask add 2 ml of 15% KI and swirl to mix. Add 0.5 ml of 40% SnCl_2 , swirl to mix, and allow to stand for 15 minutes to reduce the arsenic to the trivalent form.
8. Add to the generator flask 7 g of zinc, and close the flask immediately.

9. Heat the flask in a beaker of hot tap water, and allow the reaction to proceed for 30 minutes. A soluble red complex should form.
10. Transfer the arsine absorbing solution to a 1-cm cell, and read the absorbance at 560 nm, using unreacted silver diethyldithiocarbamate as a blank.
11. Prepare working standards in the range of 1-20 µg/ml arsenic from the stock standard.
12. Pipet 1 ml of each working standard into arsine generators, add 20 ml of distilled water and 5 ml HCl, and proceed with Step 6 of the procedure.
13. Draw a calibration curve of absorbance versus µg As, and use it to determine the arsenic content of the samples.

CALCULATIONS

$$\begin{aligned}
 \text{mg As/L urine} &= \frac{\mu\text{g As (from curve)}}{\text{ml of urine}} \\
 \text{mg As/L water} &= \frac{\mu\text{g As}}{\text{ml of water}} \\
 \text{mg As/m}^3 &= \frac{\text{mg As}}{\text{m}^3 \text{ of air sampled at STP}} \quad \text{or} \\
 &= \frac{\mu\text{g As}}{\text{liters of air sampled at STP}}
 \end{aligned}$$

REFERENCES

1. Standard Methods for the Examination of Water and Wastewater (16th ed; Washington, DC: American Public Health Association, 1985), p. 187.
2. J.L. Monkman, "Determination of Arsenic in Air," Analytical Methods Manual (Cincinnati, OH: American Conference of Government Industrial Hygienists, 1958).

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QUALITATIVE ANALYSIS OF BULK ASBESTOS

ABSTRACT

Asbestos is defined as one of a group of fibrous, hydrated mineral silicates, consisting of three main types: chrysotile, a magnesium silicate which makes up 90-95% of the asbestos used in industry; amosite, a magnesium/iron silicate; and crocidolite, a sodium/iron silicate. The material was widely used for insulation and reinforcement in years past, but is currently considered a serious respiratory health hazard and potential carcinogen. For that reason, samples are prepared in a HEPA-filtered workstation.

Polarized light microscopy (PLM) is used to identify the presence of asbestos fibers in bulk samples. Initial samples should consist of a core through the cross section of the material being sampled.

APPLICATIONS AND LIMITATIONS

The advantages of polarized light microscopy in the identification of asbestos fibers are (1) that the technique is very sensitive (parts-per-million range); (2) that it is fairly rapid, requiring only 1-5 minutes to complete; and (3) that individual types of asbestos can be identified, using supplementary techniques (see Reference 1).

The disadvantages include (1) that, in order to be seen, the particles must be at least 0.5 μm in the smallest direction; and (2) that the analyst needs more competence and experience in this technique than in many others. The first disadvantage is mitigated somewhat by the fact that hazardous particles are defined as those having the following characteristics: length $>5 \mu\text{m}$, diameter $<3 \mu\text{m}$, and aspect ratio (length:width) $>5:1$. Thus, particles not visible by PLM are believed to be relatively harmless.

One additional limitation to the technique is the presence of non-asbestos fibers in many insulation materials. The fibers found in most insulating materials have the following characteristics:

Asbestos	Straight bundles or unraveled "rope"
Fiberglass/glass wool	Clear tubes or glassy blobs
Mineral wool	Curled tubes
Cellulose/wood/paper	Cells and nuclei
Metal fragments	Opaque

In addition, binder materials, such as plaster of Paris, mortar, cement, or gypsum, can obscure the presence and/or identity of any fibers.

ES&H NOTES

Asbestos is designated as a Class A1 carcinogen by the ACGIH and a Class 1 carcinogen by the IARC. Suspected asbestos-containing materials shall be prepared in a HEPA-filtered workstation. The room and/or hood shall be clearly labeled with a sign indicating that a carcinogen is in use.

APPARATUS

Polarized Light Microscope, Bausch & Lomb

Microscope slides, glass

Tweezers and teasing needles

REAGENTS

Index of refraction liquid, Cargille High Density, certified. The preferred index of refraction is 1.552, but either 1.550 or 1.554 is also acceptable.

ANALYTICAL PROCEDURE

1. Working in a HEPA-filtered workstation, clean a glass microscope slide; and apply a drop of Cargille index of refraction liquid.
2. Remove typical fibers from the sample, and deposit them in the liquid on the slide.
3. Mount the slide on the polarizing light microscope, turn on the illuminator, and examine the fibers. Asbestos fibers usually look like straight bundles or unraveled rope.
4. Rotate the polarizer until the background appears dark. Rotate the stage, observing the fibers for color change to red-brown or blue-green. The color change is common for asbestos, although its presence doesn't guarantee that the sample is asbestos nor does its absence guarantee that it isn't. The polarizer also helps blank out some of the binder materials, thus emphasizing the fibers. Reference 1 contains photomicrographs of asbestos and other associated materials, which can be used to help identify the sample.

REFERENCES

1. W.C. McCrone, The Asbestos Particle Atlas (Ann Arbor, MI: Ann Arbor Science, 1980).
2. Asbestos-Containing Materials in School Buildings: A Guidance Document. Part 1 (Washington, DC: U.S. Environmental Protection Agency, 1979).
3. M. Cossette, "Defining Asbestos Particulates for Monitoring Purposes," Definitions for Asbestos and Other Health-Related Silicates, ASTM Publication 834, ed B. Levadie (Philadelphia: American Society for Testing and Materials, 1984), p. 5.
4. "Asbestos (Bulk)," NIOSH Manual of Analytical Methods, Vol. 1, U.S. Department of Health and Human Services Publication No. 84-100, ed P.M. Eller (3rd ed; Washington, DC: U.S. Government Printing Office, 1984), Method 9002.

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GENERAL PROCEDURES FOR ATOMIC ABSORPTION SPECTROSCOPY

ABSTRACT

The atomic absorption spectrophotometer is the instrument of choice for quantitating PPM to PPB amounts of metals in air samples, biological samples, commercial products, swipes, and water. Its advantages are (1) ease of sample preparation -- normally, only sample dissolution is required; (2) sensitivity -- most metallic elements are easily quantitated in the PPM to PPB range; (3) selectivity -- with very rare exceptions, the sensitive lines of one element do not overlap the sensitive lines of another; and (4) minimum matrix interferences -- if present, procedures for elimination of these interferences are listed in Table B-2.**

This atomic absorption section contains divisions which describe the equipment, sample preparation, reagents, data collection, and calculations. Standardization techniques closely follow the manufacturer's instructions in the AA Methods Manual. For installation, operating procedures, and safety precautions, see Reference 3.

APPLICATIONS AND LIMITATIONS

1. The analytical working range for each metal is given in Table B-2. Higher concentrations can be determined by dilution of the sample.
2. The detection limits and interferences for each metal are given in Table B-2.
3. The coefficient of variation for the analysis is approximately 2%, depending upon the instrument and the absorbance of the sample.
4. As, In, Se, Te, Tl, and Hg are very volatile elements and must not be heated any more than necessary in sample preparation.

ES&H NOTES

Some of the metals determined by AA are designated as carcinogens by the ACGIH and by the IARC. These materials should be handled in a Designated Area, typically a laboratory hood, to minimize respiratory exposure. The room and/or hood shall be clearly labeled with a sign indicating that a carcinogen is in use.

** See Reference 1, herein referred to as the AA Methods Manual.

Because hydrofluoric acid is highly toxic and corrosive, avoid inhalation, ingestion, or contact. Wear appropriate gloves and handle in a hood. Wash skin after use to avoid potential tissue damage.

APPARATUS

Atomic absorption spectrophotometer - Perkin-Elmer Model 703, including the necessary burner heads for air-acetylene and nitrous oxide-acetylene flames and the appropriate hollow cathode (HCL) or electrodeless discharge (EDL) lamps.

Recorder, Texas Instruments "Servo-Riter," 0-10 mv

Atomic absorption accessories - See the AA Methods Manual for Delves sampling cup, boat method, graphite furnace, flameless mercury analyzer, hydride generator, etc.

Beakers, 100 and 150 ml, with watchglass covers

Graduated cylinders, 10 ml and 100 ml

Hot plate capable of reaching 400°C

Platinum crucibles

Polyethylene bottles, 125 ml and 150 ml

Teflon beakers

REAGENTS

Nitric acid, conc. (70% HNO_3), redistilled

Sulfuric acid, conc. (96% H_2SO_4)

Perchloric acid, conc. (70% HClO_4)

Acid digestion mixture I, 8:1:1 of conc. HNO_3 : conc. H_2SO_4 : conc. HClO_4

Hydrochloric acid, conc. (36% HCl)

Hydrochloric acid (6N) - Add 500 ml of conc. HCl to 500 ml of distilled water.

Hydrofluoric acid (48% HF)

Hydrogen peroxide (30% H_2O_2)

Stock standards - Commercially prepared aqueous stock standards of 1000 µg/ml are available for most elements. Alternatively, make up 1000-µg/ml solutions of each of the elements listed in Table B-2, being sure to acidify them properly to keep the metals in solution (see Reference 4 or 5). As, Be, Bi, and Sb are easily hydrated to their insoluble oxychlorides or hydroxides; therefore the stock solutions of these elements must be in at least 6N acid. Others are stable in 1N acid. Keep all stock solutions in polyethylene bottles. Hg and Tl form insoluble chlorides in their lower oxidation states; therefore add 5 ml of conc. HNO₃, prior to dilution to volume, to provide an oxidizing medium and ensure their higher valence states.

Working solutions - From each of the 1000-µg/ml stock standards, prepare working standards to cover the range for each metal as given in Table B-2. All working standards should be acidified as strongly as the stock standards and stored in polyethylene bottles. Remake the standards every day for best results. When analyzing for any of the metals with known interferences, as indicated in Table B-2, prepare the standards according to the "Remedies" listed in the Table.

SAMPLE PREPARATION

Air samples and swipes

1. Transfer samples to beakers. Check Reference 1 for the optimum dissolution acids.
2. For most samples containing metals other than Be, add 5 ml of conc. HNO₃. Heat on a hot plate in a fume hood until the sample chars or until about 1 ml of a colorless or light yellow solution remains. If necessary to prevent loss of sample, cover each beaker with a watchglass.
3. Cool the sample. If it remains light colored and clear, transfer it to a 10-ml graduated cylinder with distilled water. Dilute the aliquots, if necessary, or reduce the volume by evaporation to obtain a concentration within the working range of the metal.
4. If the sample is dark yellow or undissolved particulates remain, add more conc. HNO₃, and continue as in Step 2. Undissolvable particulates may be allowed to settle in the graduated cylinder or may be filtered through a No. 41 filter. In addition, some metals should be heated to near dryness and redissolved in 6N HCl (see Reference 1).

5. For samples containing BeO, add 5-10 ml of acid digestion mixture I. Heat the samples at 200-400°C until digestion is complete and white SO₃ fumes are evolved. Proceed as in Step 3.

Ores, soils, and dusts

1. Ignite a 1.0000 ± 0.005 g dried 200-mesh sample in a platinum crucible at 900°C. Cool and transfer the ignited sample to a 100-ml Teflon beaker.
2. Dissolve the sample by adding 10 ml of HF and 10 ml of HCl, and evaporate to dryness on a low-temperature hot plate. Repeat the addition of HF and HCl, and evaporate to dryness.
3. Add 5 ml of HCl, and evaporate to dryness. Repeat.
4. Dissolve the residue in 6N HCl or conc. HNO₃, and quantitatively transfer it to a 100-ml graduated cylinder with distilled water. Dilute the aliquots, if necessary, to obtain metal concentrations within the working range of the method.

Vegetation

1. Place several grams of dried vegetation in a blender, and blend until the sample is thoroughly cut and mixed.
2. Place about 10 g in a platinum or porcelain crucible, and heat in a muffle furnace at 450°C until a white ash remains.
3. Continue with Step 1 under Soils.

Urine

1. Add 20 ml of conc. HNO₃ and 5 ml of H₂O₂ to a 100-ml aliquot of urine in a 500-ml Erlenmeyer flask.
2. Evaporate to dryness; repeat the addition of conc. HNO₃ until a white ash is obtained.
3. Add 5 ml of conc. HNO₃ or 6N HCl. Warm the solution to dissolve the residue, and quantitatively transfer it to a 10- ml graduated cylinder.

ANALYTICAL PROCEDURE

1. Turn on the power to the atomic absorption unit. Install the lamp to be used, and adjust the lamp current to the recommended setting.

2. Turn on the air and the acetylene or nitrous oxide to the control box; and adjust the fuel and air flow, as indicated in the instruction Manual.
3. Install the proper burner head, according to the "type of oxidant," as listed in Table B-2.
4. Set the wavelength control to the proper analytical wavelength for the metal of interest. Adjust the GAIN to approximately two-thirds of full scale.
5. Turn on the fuel flow to the burner and ignite. Tune the burner and the nebulizer flow to maximize the absorption. Aspirate a series of standards and the samples, and record the absorbance.
6. Prepare a calibration curve by plotting on linear graph paper the absorbance versus concentration of each standard in $\mu\text{g/ml}$. From the calibration curve, read the concentration ($\mu\text{g/ml}$) of the samples. Blank values, if any, are subtracted from each sample.
7. Alternatively, calculate the concentration using the "CURVE" program on the STANDARD PAC disk for the Hewlett-Packard HP-85 calculator.

ALTERNATE TECHNIQUES FOR SAMPLE INTRODUCTION

There are several alternative sample introduction techniques which can improve the sensitivity and detection limits of atomic absorption for certain elements (see Table B-3).

Hydride generation is a technique used to determine very low concentrations of elements forming gaseous hydrides, i.e., As, Bi, Ge, Sb, Se, Sn, and Te. A sample reacts with sodium borohydride to generate the gaseous hydride, which is collected until the reaction ceases. The gases are then swept into the flame, and the response is recorded on a chart recorder. Detection limits generally improve by a factor of 10 to 10,000, depending upon the element.

The graphite furnace is a flameless sampling device providing extremely low detection limits of 10^{-10} to 10^{-12} g for most metals. In the furnace, unwanted solvent and matrix materials are vaporized first, using temperature programming, and then purged. Atomization then occurs in an inert atmosphere. Sensitivity and detection limits are improved by a factor of 100 to 1000 because of longer residence time in the light path, eliminating the need for some preconcentration techniques. In addition to small samples, the technique is compatible with both solid samples and those only partially dissolved. (See "Total Lead and Copper in Drinking Water" and "Thallium in Urine," Section B of this Manual.)

CALCULATIONS

1. Air sample: $\text{mg/m}^3 = \frac{\text{ml solution}}{1000} \times \frac{\mu\text{g/ml}}{\text{vol air sample, m}^3}$
2. Swipe: $\text{mg} = \frac{\text{ml solution} \times \mu\text{g/ml}}{1000}$
3. Liquid: $\% = \frac{\mu\text{g/ml}}{10,000}$
4. Solid: $\% = \frac{\text{ml solution} \times \mu\text{g/ml}}{\text{wt original sample (g)} \times 10,000}$

REFERENCES

1. Analytical Methods for Atomic Absorption Spectrophotometry, Publication No. 0303-0152 (Norwalk, CT: The Perkin-Elmer Corp., 1982).
2. Analytical Methods for Atomic Absorption Spectrophotometry (Norwalk, CT: The Perkin-Elmer Corp., 1976).
3. Instructions for Model 703 Atomic Absorption Spectrophotometer, Publication No. 993-9454 (Norwalk, CT: The Perkin-Elmer Corp., 1978).
4. A.F. Ward, "Stock Standard Preparation," Jarrell-Ash Plasma Newsletter 1(2):14 (1978).
5. Techniques in Graphite Furnace Atomic Absorption Spectrophotometry Publication No. 0993-8150 (Norwalk, CT: The Perkin-Elmer Corp., 1985).
6. Analytical Methods for Furnace Atomic Absorption Spectroscopy, Publication No. B010-0108 (Norwalk, CT: The Perkin-Elmer Corp., 1981).

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TABLE B-2
ATOMIC ABSORPTION PARAMETERS

ELEMENT	ANALYTICAL WAVELENGTH (nm)	DETECTION LIMIT (ug/ml)	UPPER RANGE OF LINEARITY (ug/ml)	TYPE OF OXIDANT	INTERFERENCES	REMEDY
As	328.1	.002	4.0	Oxidizing Air	IO ₃ ⁻ , MnO ₄ ⁻ , WO ₄ ⁻² ; Mineral acids; Al; Acetic acid	(1)
As	309.3	.03	100	Reducing N ₂ O	Ionization Fe, V, Ti; Acetic acid; HCl, H ₂ SO ₄	(2) (3)
As	193.7 (EDL)	.2	100	Reducing Air	>1% Salt content	(4)
Au	242.8	.01	50	Oxidizing Air	Strong mineral acids; CN ⁻ Noble metals	(3) (5)
B	249.7	.7	400	Reducing N ₂ O	None	
Ba	553.6	.009	20	Reducing N ₂ O	High conc. of Ca Ionization	(4) (2)
Be	234.9	.001	1.0	Reducing N ₂ O	High conc. of Al, Si, Mg	(3)
B+	223.1 (Doublet)	.04	20	Oxidizing air	None	
Ca	422.7	.002	5.0	Oxidizing Air	Ionization Si, Al, Be, P, Ti, V	(2) (6)
Cd	228.8	.001	2.0	Oxidizing Air	None	

<u>ELEMENT</u>	<u>ANALYTICAL WAVELENGTH (nm)</u>	<u>DETECTION LIMIT (ug/ml)</u>	<u>UPPER RANGE OF LINEARITY (ug/ml)</u>	<u>TYPE OF OXIDANT</u>	<u>INTERFERENCES</u>	<u>REMEDY</u>
Co	240.7	.01	3.5	Oxidizing Air	High conc. of heavy metals	(3)
Cu	324.7	.002	5.0	Oxidizing Air	None	
Dy	404.6	*.05	50	Reducing N ₂ O	Ionization H ₂ SO ₄ , H ₃ PO ₄ Other Lanthanides	(2) (3)
Er	400.8	*.04	40	Reducing N ₂ O	Ionization	(2)
Eu	459.4	*.02	200	Reducing N ₂ O	Ionization Other Lanthanides	(2)
Fe	248.3	.004	5.0	Oxidizing Air	Ni, Co, Cu	(3) or (8)
Ga	287.4	*.05	100	Reducing N ₂ O	Ionization	(2)
Gd	368.4	*1.2	-	Reducing N ₂ O	Ionization Other Lanthanides	(2)
Ge	265.1 (Doublet)	*.1	200	Reducing N ₂ O	None	
Hf	286.6	*2	-	Reducing N ₂ O	Possible oxide formation	(9)

ELEMENT	ANALYTICAL WAVELENGTH (nm)	DETECTION LIMIT (µg/ml)	UPPER RANGE OF LINEARITY (µg/ml)	TYPE OF OXIDANT	INTERFERENCES	REMEDY
Hg	253.7	.28	200	Oxidizing Air	Large conc. of Co	(3)
Hc	410.7	*.04	50	Reducing N ₂ O	Ionization Other Lanthanides	(2)
Ir	303.9	*.02	80	Oxidizing Air	Excess Al, Mg, Cu, Zn; PO ₄ ⁻³	(3)
Ir	264.0	*.6	-	Reducing Air	Al, La; Other common elements	(3)
K	766.5	.002	2.0	Oxidizing Air	Ionization Strong mineral acids	(10) (3)
La	550.1	*2	1000	Reducing N ₂ O	Ionization Other Lanthanides	(2)
Li	670.8	.0008	3.0	Oxidizing Air	Ionization	(2)
Lu	336.0	*.7	6.0	Reducing N ₂ O	Ionization Other Lanthanides	(2)
Mg	285.2	.00001	0.5	Oxidizing Air	High conc. of Si, Al, Ti, P	(6) or (11)
Mn	279.5	.002	2.0	Oxidizing Air	Si	(12)
Mo	313.3	.03	40	Reducing N ₂ O	Ca, Sr, Fe; SO ₄ ⁻²	(13)
Na	589.0 (Doublet)	.0002	1.0	Oxidizing Air	Ionization High conc. of mineral acids	(2) or (14) (3)

ELEMENT	ANALYTICAL WAVELENGTH (nm)	DETECTION LIMIT (µg/ml)	UPPER RANGE OF LINEARITY (µg/ml)	TYPE OF OXIDANT	INTERFERENCES	REMEDY
Ni	334.4	1.0	600	Reducing N ₂ O	Possible oxide formation	(9)
Ni	482.6	*1.0	200	Reducing N ₂ O	Ionization Other Lanthanides, esp. Pr Excess Si, Al, Ce; F ⁻	(2) (3)
Ni	332.6	.009	2.0	Oxidizing Air	High conc. of Fe, Cr	(3)
Os	290.9	.08	-	Reducing N ₂ O	None	
P	213.6 (Doublet)	50	10,000	Reducing N ₂ O	None	
Pb	283.3	.03	20	Oxidizing Air	Large excess of other elements (3) or (4)	
Pb	242.9	*.02	10	Oxidizing Air	Al, Co, Ni, Pt, Rh, Ru	(15)
Pb	495.1	*5.0	-	Reducing N ₂ O	Ionization Other Lanthanides	(2)
Pt	265.9	.07	60	Oxidizing Air	High conc. of many metals and acids	(16)
Rb	780.0	*.002	5.0	Oxidizing Air	Ionization Al; Strong mineral acids	(2) (3)
Re	346.0	*.5	500	Reducing N ₂ O	xs Al, Ca, Fe, Pb, Mn, Mo, K	(3)

<u>ELEMENT</u>	<u>ANALYTICAL WAVELENGTH (nm)</u>	<u>DETECTION LIMIT (µg/ml)</u>	<u>UPPER RANGE OF LINEARITY (µg/ml)</u>	<u>TYPE OF OXIDANT</u>	<u>INTERFERENCES</u>	<u>REMEDY</u>
Rh	343.5	*.004	15	Oxidizing Air	Precipitation Chemical	(17) (18)
Ru	349.9	*.07	20	Oxidizing Air	Precipitation Mo, Pt, Rh, La; HCl	(17) (6)
Sb	217.6	.05	30	Oxidizing Air	None	
Sc	391.2	*.02	25	Reducing N ₂ O	Ionization S-2, Fe-	(2) (3)
Se	196.0 (EDL)	.13	200	Oxidizing Air	Background scattering	(4)
Si	251.6	.06	150	Reducing N ₂ O	Fe when using multi-element lamp with Fe line precipitation	(19) (20)
Sm	423.2	*2.0	400	Reducing N ₂ O	Ionization Other Lanthanides	(2)
Sn	286.3	.11	400	Reducing N ₂ O	None	
Sr	460.7	*.002	5.0	Reducing N ₂ O	Ionization Chemical	(2) (6)
Ta	271.5	1.0	-	Reducing N ₂ O	Possible oxide formation	(9)
Tb	432.6	*.6	200	Reducing N ₂ O	Ionization Other Lanthanides	(2)

ELEMENT	ANALYTICAL WAVELENGTH (nm)	DETECTION LIMIT (µg/ml)	UPPER RANGE OF LINEARITY (µg/ml)	TYPE OF OXIDANT		INTERFERENCES		REMEDY
Te	214.3	.04	20	Oxidizing Air		Excess Ca, Si, Na, Zn		(3)
Ti	364.3	.05	100	Reducing N ₂ O		Ionization Signal increased by many metals		(2) (3)
Tl	276.8	.02	40	Oxidizing Air		None		
Tm	371.8	*.01	60	Reducing N ₂ O		Ionization Other Lanthanides		(2)
U	351.5	11.0	-	Reducing N ₂ O		Ionization Excess Al, Co, Fe, Pb, Ni		(2) (3)
V	318.4 (Triplet)	.04	200	Reducing N ₂ O		Ionization Excess Fe, Al, Ti; H ₃ PO ₄		(2) (3)
W	255.1	1.2	500	Reducing N ₂ O		Excess Fe in acid		(3)
Y	410.2	*.05	50	Reducing N ₂ O		Ionization Some mineral acids		(2) (3)
Yb	398.8	.005	15	Reducing N ₂ O		Ionization Other Lanthanides		(2)
Zn	213.9	.002	1.0	Oxidizing Air		None		
Zr	360.1	.4	600	Reducing N ₂ O		Possible oxide formation		(9)

*Value listed in 1976 version of Reference 1 only.

REMEDIES

1. Remove interfering substances or matrix match.
2. Add 0.1% alkali salt (i.e., KCl) to samples and standards.
3. Matrix match samples and standards.
4. Background correction at 194.2 nm (Hg).
5. Addition of Cu may reduce the interference.
6. Add 0.1-1.0% La to samples and standards.
7. Add 200 ppm Fe to samples and standards. Add Ni in an amount equal to the amount of Cr in each standard. Add Ca to overcome signal depression by phosphate.
8. Add 200 ppm Ni, Co, and/or Cu to both samples and standards.
9. Inverse calibration curves result at high concentrations. To improve sensitivity and linearity, add 0.2% Al and 1% HF to samples, standards, and blanks.
10. Add Na to a ratio of 2 parts Na to each part K in samples and standards.
11. Due to the high sensitivity of Mg and the effect of sample dilution, these interferences should present few problems.
12. Add 0.2% CaCl_2 to overcome signal depression by Si.
13. Add 0.1% Al to samples and standards.
14. Add K at a ratio of 2 parts K to each part Na in samples and standards.
15. Add 0.5% La or 0.01M EDTA to samples and standards.
16. Add 0.2% La in 1% HCl to samples and standards.
17. Add 10% HCl to prevent Rh precipitation; 20% for Ru.
18. Add 1% Na_2SO_4 to control chemical interferences and improve linearity and sensitivity.
19. Use a secondary silicon resonance line such as 250.7, 252.8, or 252.4 nm.
20. Add 0.1% HF to prevent precipitation of Si.

TABLE B-3
TYPICAL AA DETECTION LIMITS^(a)
($\mu\text{g/ml}$)

ELEMENT	FLAME AA	GRAPHITE FURNACE AA	HYDRIDE GENERATION	MICROSAMPLING ^(b)
As	0.1	0.0002	0.00002	0.02
Bi	0.02	0.0001	0.00002	0.003
Cd	0.005	0.000003	-	0.00005
Ge	0.10	-	0.01	-
Hg	0.2	0.002	-	-
Pb	0.01	0.00005	-	0.001
Sb	0.03	0.0002	0.0001	-
Se	0.07	0.0005	0.00002	0.01
Sn	0.1	0.0002	0.0002	-
Te	0.02	0.0001	0.00002	0.01
Tl	0.009	0.0001	-	0.001
Zn	0.0008	0.000001	-	0.00003

(a) See Reference 1

(b) See the 1976 Version of Reference 1

CHLORINE IN AIR, WATER, AND WASTEWATER

ABSTRACT

A red color develops when DPD reacts with chlorine in acid or alkaline solutions. The maximum absorption is at 530 nm.

APPLICATIONS AND LIMITATIONS

This method registers the total available chlorine and is rapid and simple. Bromine, iodine, ozone, and oxidized forms of manganese and chromium also may react and read as chlorine. The range is 0-1.7 mg/L. Higher concentrations can be analyzed by diluting the sample.

APPARATUS

Hach colorimeter, Model DREL/5

Fritted bubbler or midget impinger, all-glass

Assorted laboratory glassware

REAGENTS

Sodium hydroxide (0.01N) - Dissolve 0.4 g of NaOH in 1 liter of distilled water.

Sulfuric acid (1N) - Add 3 ml of conc. H_2SO_4 to 97 ml of water.

Hach DPD Total Chlorine Reagent Powder Pillows, Cat. No. 14064-99

ANALYTICAL PROCEDURE

1. Pass a known volume of air through a fritted bubbler or a midget impinger containing 0.01N NaOH. After sampling, neutralize to pH 7.0 with 1N H_2SO_4 .
2. Fill a 25-ml colorimeter bottle with air sampling solution or water to be analyzed.
3. Add the contents of one DPD Total Chlorine Reagent Powder Pillow, and mix well.

4. Allow 5 minutes for color development at 20°C. If chlorine is present, a red color will develop.
5. Fill a colorimeter cell with an untreated water sample, and place it in the cell holder. Insert the Chlorine (DPD Method) Meter Scale in the meter, and adjust the Wavelength Dial to 530 nm.
6. Set the Mode Switch to LEFT SET, and check the left set adjustment. If necessary, adjust the LEFT SET control to align the meter needle with the extreme left mark on the meter scale arc.
7. Set the Mode Switch to NORM, and adjust the RIGHT SET controls for a meter reading of zero mg/L.
8. Place the prepared sample in the cell holder. Read the mg/L chlorine.
9. If the sample temporarily turns yellow when adding the DPD Total Chlorine Reagent or reads above the 1.7 mg/L mark, the chlorine concentration is too high for the meter scale; and a sample dilution is necessary. A slight loss of chlorine may occur due to the dilution.

REFERENCES

1. Water Analysis Handbook (Loveland, CO: Hach Co., 1984), p. 2-64.

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HEXAVALENT CHROMIUM IN AIR AND WATER

ABSTRACT

Hexavalent chromium reacts with 1,5-diphenylcarbohydrazide to produce a purple color absorbing at 540 nm.

APPLICATIONS AND LIMITATIONS

The range for this method is 0-0.5 mg/L. Mercurous and mercuric ions interfere slightly. Iron, in amounts greater than 1 mg/L, interferes by producing a yellow color. Vanadium interferes in the same manner, but may be overcome by waiting 10 minutes before reading.

APPARATUS

Hach colorimeter, Model DREL/5

Graduated cylinders, 25 ml

Midget impingers, all glass

REAGENTS

Sodium hydroxide (1N) - Dissolve 40 g of NaOH in 1 liter of distilled water.

Nitric acid (1:1)

Hach ChromaVer 3 Chromium Reagent Powder Pillows
(1,5-diphenylcarbohydrazide), Cat. No. 12066-66

ANALYTICAL PROCEDURE

1. Collect samples in two midget impingers in series, using 15 ml of 1N NaOH as the collecting medium in each impinger.
2. Transfer the samples to a 25-ml graduated cylinder. Acidify with (1:1) nitric acid to pH 4, and dilute to volume.
3. Place a 5-ml aliquot into a 25-ml sample cell, and dilute to 25 ml with distilled water. Alternatively, take a water sample by filling a clean sample cell to the 25-ml mark.

4. Add the contents of one ChromaVer 3 Chromium Reagent Powder Pillow, and swirl to mix. A purple color will develop if hexavalent chromium is present. Allow at least 5 minutes for the color to develop fully, but do not wait more than 20 minutes.
5. Fill a clean sample cell to the 25-ml mark with the original water sample, and place it in the cell holder. Insert the Chromium, Hexavalent (ChromaVer 3 Method) Meter Scale into the meter, and adjust the Wavelength Dial to 540 nm.
6. Set the Mode Switch to LEFT SET, and check the left set adjustment. If necessary, adjust the LEFT SET control to align the meter needle with the extreme left mark on the meter scale arc.
7. Set the Mode Switch to NORM, and adjust the RIGHT SET controls for a meter reading of zero mg/L.
8. Place the prepared sample in the cell holder. Read the mg/L hexavalent chromium. The results can be expressed as mg/L chromate or as mg/L sodium chromate by multiplying the mg/L hexavalent chromium reading by 2.23 or 3.12, respectively.

REFERENCES

1. Water Analysis Handbook (Loveland, CO: Hach Co., 1984), p. 2-73.

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COMPRESSED BREATHING AIR

ABSTRACT

This method describes the analytical techniques used in analyzing compressed breathing air. The specification requirements are listed by the Compressed Gas Association, Inc., 500 Fifth Avenue, New York, NY. Table B-4 lists the CGA Specification G-7.1 (1966). Grade D gas is the breathing air used at Sandia Laboratories.

TABLE B-4

COMPRESSED GAS ASSOCIATION SPECIFICATIONS

LIMITING CHARACTERISTICS	GRADE A	GRADE B	GRADE C	GRADE D
%O ₂ (v/v). Balance mainly N ₂ (Note 1)	Atm.	Atm.	Atm./ 19/23	Atm./ 19-23
Water		None condensed	Note 2	Note 2
Hydrocarbons (condensed) in mg/m ³ of gas at STP		None	5	5
Carbon monoxide			50	20
Carbon dioxide				1000

Note 1: The term "Atm." (atmospheric) denotes the O₂ content normally present in atmospheric air (~21%); the numerical values denote the O₂ limits for synthesized air.

Note 2: The water content of compressed air required for any particular grade may vary with the intended use from saturated to very dry. If a specific water limit is required, it should be specified as a limiting dewpoint or concentration in PPM (v/v). Dewpoint is expressed in temperature (°F) at 1 atmosphere absolute pressure (760 mm Hg).

ANALYTICAL PROCEDURE

1. Percent Oxygen should be determined by (a) an apparatus employing a comparison tube filled with a color-reactive chemical, or by (b) a gas chromatograph. The technique used must be specific for oxygen.
2. Water content should be determined by one of the following techniques: (a) For a qualitative analysis, support the cylinder in an inverted position (valve at the bottom) for 5 minutes. The cylinder and its contents should be at room temperature (22°C). Open the cylinder valve slightly (USE CAUTION!) while the cylinder remains inverted, and vent the air with a barely audible flow into an open dry container for one minute. (CAUTION: A rapid gas flow may cause any liquid to disperse and not collect in the container.) Any water in the breathing air will condense on the dry container. (b) Alternatively, use a gas chromatograph.
3. Condensed Hydrocarbon content should be determined by one of the following techniques: (a) For a qualitative analysis, support the cylinder in an inverted position (valve at the bottom) for 5 minutes. The cylinder and its contents should be at room temperature (22°C). Open the cylinder valve slightly (USE CAUTION!) while the cylinder remains inverted, and vent the air with a barely audible flow into an open dry container for one minute. (CAUTION: A rapid gas flow may cause any liquid to disperse and not collect in the container.) Any oil in the breathing air will condense on the dry container. Alternatively, (b) scrub the air sample with spectral-grade carbon tetrachloride and examine by an IR, or (c) use a gas chromatograph.
4. Carbon Monoxide content should be determined by (a) a gas-cell equipped infrared analyzer, calibrated at 4.6 microns with appropriate calibration gas standards; or by (b) a gas chromatograph specific for carbon monoxide.
5. Odor should be checked directly by smelling of a moderate flow of air from the container being tested. The presence of a pronounced odor should render the air unsatisfactory for breathing purposes.
6. Carbon Dioxide content should be determined by (a) a gas-cell equipped infrared analyzer, calibrated at 4.3 microns with appropriate calibration gas standards; or by (b) a gas chromatograph specific for carbon dioxide.
7. Gaseous Hydrocarbon content should be determined by (a) a gas chromatograph with a flame ionization detector, calibrated with methane gas standards; or by (b) a gas-cell equipped infrared analyzer, calibrated at 3.5 microns with methane standards.

8. Nitrogen Dioxide content should be determined by (a) a gas-cell equipped infrared analyzer, calibrated at 6.2 microns with appropriate gas standards; or by (b) a suitable colorimetric method (see "Nitrogen Dioxide in Air," Section B of this Manual).
9. Sulfur Dioxide content should be determined by (a) a gas-cell equipped infrared analyzer, calibrated at 7.3 microns with appropriate gas standards; or by (b) a suitable colorimetric method (see "Sulfur Dioxide in Air," Section B of this Manual).
10. Halogenated Solvent content should be determined by (a) a gas chromatograph or by (b) a gas-cell equipped infrared analyzer.
11. Acetylene content should be determined by a gas-cell equipped infrared analyzer, calibrated at 13.7 microns with appropriate gas standards.

REFERENCES

1. Commodity Specification for Air, CGA Specification G-7.1 (New York: Compressed Gas Association, Inc., 1966).
2. Methods of Air Sampling and Analysis, ed J. P. Lodge, Jr. (3rd ed; Chelsea, MI: Lewis Publishers, 1989).

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CYANIDES AND HYDROCYANIC ACID IN AIR AND WATER

(Colorimetric Method)

ABSTRACT

Cyanide is neutralized and converted to cyanogen chloride by reaction with chloramine-T. This reacts with pyridine-pyrazolone reagent to form a blue color, which can be read at 630 nm.

APPLICATIONS AND LIMITATIONS

Sensitivity and precision can be improved by extracting the aqueous solution with n-butyl alcohol and then reading the absorbance at 630 nm. For aqueous color readings, the effective range is 1-5 μg and sensitivity is 0.5 μg . For the extracted color, the range is 0.2-2.0 μg , while the sensitivity is 0.1 μg .

Only minor limitations occur with this method. The salt content of sample and standards should be the same to obtain colors of comparable intensity. Thiocyanates and cyanogen will give the same reaction as cyanides.

ES&H NOTES

Phenylhydrazine is designated as a Class A2 carcinogen by the ACGIH. Solid cyanides are highly toxic by ingestion. These materials should be handled in a Designated Area, typically a laboratory hood. The room and/or hood shall be clearly labeled with a sign indicating that a carcinogen is in use. Wash hands well after handling.

APPARATUS

Spectrophotometer, Hewlett-Packard Model 8450A, for use with 1-cm cells at 620-630 nm

Fritted bubbler

Assorted laboratory glassware

REAGENTS

Sodium hydroxide (1N) - Dissolve 40 g of NaOH in 1 liter of distilled water.

Sodium hydroxide (0.2N) - Dissolve 8 g of NaOH in 1 liter of distilled water.

Acetic acid, conc.

Acetic acid, 1:4

Chloramine-T solution - Dissolve 1 g in 100 ml of distilled water. PREPARE FRESH DAILY

3-Methyl-1-phenyl-5-pyrazolone solution, Eastman 1397 or equivalent - Prepare a saturated solution in warm water (≈ 0.5 g/125 ml water).

Ethyl alcohol (95%)

Phenylhydrazine

Bis-pyrazolone, Eastman 6969 or equivalent - Dissolve 17.4 g of 3-methyl-1-phenyl-5-pyrazolone in 100 ml of ethyl alcohol. Add 25 g of phenylhydrazine, freshly distilled under reduced pressure. Reflux in an all-glass still for 10 to 12 hours. Filter while hot, wash with 95% ethyl alcohol, and air-dry.

Pyridine

Mixed pyridine-pyrazolone reagent - Mix 125 ml of saturated pyrazolone solution with a solution containing 0.025 g of bis-pyrazolone dissolved in 25 ml of pyridine. Store in a dark bottle. The mixed reagent develops a pink color on standing. PREPARE FRESH DAILY.

Disodium hydrogen phosphate solution - Dissolve 5 g of anhydrous Na_2HPO_4 in 100 ml of distilled water.

n-Butyl alcohol

Cyanide stock standard (1 mg CN/ml) - Dissolve 2.510 g of KCN in 1 liter of distilled water.

Cyanide working standard (1 μg CN/ml) - Dilute 10 ml of stock standard to 1000 ml with distilled water, mix, and make a second dilution by pipetting 10 ml into a 100-ml volumetric flask. PREPARE FRESH DAILY.

ANALYTICAL PROCEDURE

1. For air samples, pass a known volume of air through a fritted bubbler containing 1N NaOH. Use two bubblers in series. Sample at a rate of 1 liter/min.

2. Pipet one or more aliquots (up to about 10 ml) of the air sample absorption solution or water sample into a 25-ml graduated cylinder. Dilute to 15 ml with 0.2N NaOH, and neutralize each with 1:4 acetic acid to a pH of 6-7.
3. Add 0.2 ml of chloramine-T solution, stopper, and mix. Allow 2 minutes for the reaction to occur.
4. Add 5 ml of mixed pyridine-pyrazolone reagent, stopper, and mix. Allow 20 minutes for color to develop. Dilute to 25 ml with distilled water. Read the absorbance at 620 nm.
5. If greater sensitivity is needed, add 1 ml of disodium hydrogen phosphate and 10 ml of butyl alcohol, mix, and read the absorbance at 630 nm.
6. Prepare a blank from 15 ml of 0.2N NaOH and standards in the range of 0.2-1 µg CN. Neutralize to a pH of 6-7 with 1:4 acetic acid, and proceed as in Step 3. Plot a calibration curve of µg CN versus the absorbance of the standard.

CALCULATIONS

$$\mu\text{g CN/L} = \frac{\mu\text{g CN in sample from curve} \times 1000}{\text{ml aliquot}}$$

REFERENCES

1. J. Epstein, "Estimation of Microquantities of Cyanide," Anal Chem 19:272 (1947).
2. F.J. Ludzack, W.A. Moore, and C.C. Ruchhuf, "Determination of Cyanides in Water and Waste Samples," Anal Chem 26:1784 (1954).

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CYANIDES IN AIR

(Specific Ion Electrode Method)

ABSTRACT

Air samples, collected in NaOH via a bubbler, are analyzed with a cyanide specific ion electrode.

APPLICATIONS AND LIMITATIONS

This method is a simple alternative to the colorimetric technique (see "Cyanides and Hydrocyanic Acid in Air and Water" in Section B of this Manual). The working range is 0.5-15 mg/m³ for a 90-liter air sample, and the estimated detection limit is 2.5 µg of CN⁻.

Numerous ions interfere, including sulfide, chloride, iodide, bromide, cadmium, zinc, silver, nickel, cuprous iron, and mercury. Sulfides irreversibly poison the cyanide electrode and must be removed before analysis (see Reference 1).

ES&H NOTES

Solid cyanides are highly toxic by ingestion. They should be handled in a laboratory hood. Wash hands well after handling.

APPARATUS

pH Meter

Cyanide specific ion electrode

Reference electrode

Magnetic stirrer and stirring bars

Assorted laboratory glassware

REAGENTS

Sodium hydroxide (0.1N) - Dissolve 4 g of NaOH in 1 liter of distilled water.

Stock cyanide standard (1000 µg/ml) - Dissolve 0.250 g of KCN or 0.188 g of NaCN in 100 ml of 0.1N NaOH. PREPARE FRESH WEEKLY.

ANALYTICAL PROCEDURE

1. Dilute the samples to 50 ml with 0.1N NaOH, and transfer them to 100-ml beakers. Add a stirring bar to each beaker.
2. Prepare a series of cyanide standards by successively diluting 10 ml of the cyanide stock standard to 100 ml with 0.1N NaOH. STANDARDS SHOULD BE PREPARED FRESH DAILY.
3. Allow all solutions to equilibrate to the same temperature, taking care to avoid evaporation.
4. Immerse the cyanide and reference electrodes in 50 ml of 0.1N NaOH (sample blank) to determine the baseline reading. Turn on the magnetic stirrer and gently agitate while the potential reading stabilizes. Record the mV reading.
5. Repeat Step 4 for all sample solutions.
6. Analyze all standards as in Step 4, beginning with the lowest concentration. Prepare a calibration graph on semilog paper.
7. Determine the cyanide ion concentrations from the graph.

REFERENCES

1. "Cyanides, Aerosol and Gas," NIOSH Manual of Analytical Methods, Vol. 1, U.S. Department of Health and Human Services Publication No. 84-100, ed P.M. Eller (3rd ed; Washington, DC: U.S. Government Printing Office, 1984), Method 7904.

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FLUORIDES AND HYDROGEN FLUORIDE IN AIR AND WATER

ABSTRACT

Fluoride is determined colorimetrically by the reaction between the fluoride ion and a dark red zirconium-dye lake. As the amount of fluoride increases, the color of the dye lake becomes progressively lighter and can be measured at 580 nm.

APPLICATIONS AND LIMITATIONS

This technique obeys Beer's Law between 0.0 and 2 mg/L F^- , with a detection limit of about 0.02 mg/L.

The SPADNS method is subject to errors where interfering ions may be present. They are:

INTERFERING ION	CONC. (PPM)	ERROR, mg/L F^- *
Alkalinity (as $CaCO_3$)	5000	-0.1
Al^{+3}	0.1	-0.1
Cl^-	7000	+0.1
Fe^{+3}	10	-0.1
Hexametaphosphate ($NaPO_3$) ₆	1.0	+0.1
PO_4^{-3}	16	+0.1
SO_4^{-2}	200	+0.1

*Error at 1.0 mg/L F^-

To remove most interferences, it is necessary to distill the water sample. As these interferences are neither linear nor additive, mathematical compensation will be incorrect. The temperature of the samples and standards must be the same, or the results will be incorrect.

ES&H NOTES

Sodium arsenite is designated as a known human carcinogen by the NTP. This material should be handled in a Designated Area, typically a laboratory hood. The room and/or hood shall be clearly labeled with a sign indicating that a carcinogen is in use.

APPARATUS

Hach colorimeter, Model DREL/5

Distillation apparatus, consisting of a 1-liter round-bottom long-neck boiling flask, a connecting tube, a condenser, a thermometer adapter, and a thermometer.

Midget impinger

Assorted laboratory glassware

REAGENTS

Sodium hydroxide solution (0.1N)

Hach standard fluoride solution (1 PPM F⁻), Cat. No. 291-16

Sodium arsenite solution - Add 5 g of NaAsO₂ to 1 liter of distilled water.

Hach SPADNS fluoride reagent, Cat. No. 444-11

ANALYTICAL PROCEDURE

1. Pass a known volume of air through a midget impinger containing 0.1N NaOH. Collect in series. After sampling, transfer each air sample solution to a 25-ml graduated cylinder; and dilute with distilled water to the 25-ml mark.
2. Fill a 25-ml graduated cylinder with the water sample to be analyzed.
3. Fill a 25-ml graduated cylinder with the standard 1.0-PPM fluoride solution. (The concentration needs to match that of the sample closely.)
4. Allow the standard and unknown samples to equilibrate at room temperature.
5. If the sample contains chlorine, remove it by adding 2 drops of sodium arsenite solution. (The SPADNS reagent already contains some sodium arsenite.)
6. Pipet 5 ml of SPADNS Fluoride Reagent into each graduated cylinder, stopper, and mix well. Transfer each to colorimeter cells.
7. Insert the Fluoride (SPADNS METHOD) Meter Scale into the Hach colorimeter, and adjust the Wavelength Dial to 580 nm.

8. Set the Mode Switch to LEFT SET, and check the left set adjustment. If necessary, adjust the LEFT SET control to align the meter needle with the extreme left mark on the meter scale arc.
9. Set the Mode Switch to NORM, and adjust the RIGHT SET controls for a meter reading equal to the fluoride standard.
10. Place the prepared sample in the cell holder. Read the mg/L of fluoride.

CALCULATIONS

Total $\mu\text{g F}^-$ in sample = ($\mu\text{g/ml F}^-$) x sample volume (ml)

mg F^-/m^3 = $\mu\text{g F}^-/\text{liters of air sampled}$

mg HF/m^3 = ($\mu\text{g F}^-/\text{liters of air sampled}$) x 1.05

REFERENCES

1. Water Analysis Handbook (Loveland, CO: Hach Co., 1984), p. 2-113.
2. Standard Methods for the Examination of Water and Wastewater (16th ed; Washington, DC: American Public Health Association, 1985), p. 352.
3. "Tentative Method of Analysis for Fluoride Content of the Atmosphere and Plant Tissues (Manual Methods)," Methods of Air Sampling and Analysis, ed J.P. Lodge (3rd ed; Chelsea, MI: Lewis Publishers, 1989), Method 203.

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FLUORIDE IN URINE

ABSTRACT

Fluoride is separated directly from urine by ion exchange, then eluted and determined colorimetrically at 536 nm.

APPARATUS

Spectrophotometer, Hewlett-Packard Model 8450A

Chromatographic columns, Kontes No. K-42225 Chromaflex
Column No. 2, with 125-ml reservoir

Assorted laboratory glassware

REAGENTS

Dowex 50 W-X8, 20 to 50 mesh in the free acid form as a
urine preservative

Hydrochloric acid (3M) - Dilute one part of conc. HCl to 3
parts of distilled water.

Dowex 50 W-X8, 100 to 200 mesh in the free acid form

Ethyl alcohol

Sand, white quartz, 60 to 120 mesh

Charcoal, coconut, acid-washed, activated, 50 to 100 mesh

Dowex 1-X8, 100 to 200 mesh in the chloride form

Sodium hydroxide solution (3M) - Dissolve 120 g of NaOH in 1
liter of distilled water.

Sodium hydroxide (0.3M) - Dissolve 12 g of NaOH in 1 liter
of distilled water.

Fluoride standard (10 $\mu\text{g/ml F}^-$) - Dissolve 0.221 g of NaF in
1 liter of 0.3N NaOH.

Eriochrome Cyanine R reagent - Dissolve 1.80 g of Eriochrome
Cyanine R in 1 liter of distilled water.

Zirconium reagent - Dilute a solution of 0.265 g of $\text{ZrOCl}_2 \cdot$
 $8\text{H}_2\text{O}$ in 50 ml of water to 1 liter with conc. HCl.

Mixed color reagent - Mix equal volumes of zirconium reagent and Eriochrome Cyanine R reagent (add zirconium to dye). Five ml of this mixed reagent is required for each fraction collected.

Reference solution - To obtain the zero absorbance reading, add 10 ml of the dye solution to 100 ml of water; then add 10 ml of a solution prepared by diluting 7 ml of conc. HCl to 10 ml with water.

PREPARATION OF RESINS

Dowex 50 W-X8, 20 to 50 mesh, for urine preservation - Wash the resin in a large column with 3 volumes of distilled water; then wash with 5 volumes of 3M HCl. (Volume is that equivalent to the amount of resin.) Finally, wash with distilled water until the effluent is neutral to pH test paper. Drain the column, transfer the resin to a Pyrex tray, and dry at 40°C.

Dowex 50 W-X8, 100 to 200 mesh - In a large column, wash with 3 volumes of ethyl alcohol, 3 volumes of distilled water, and 5 volumes of 3M HCl; then wash with water until the effluent is neutral to pH test paper. Store as a 1:1 slurry in distilled water.

Sand - Digest at 100°C for 2 hours with 20% NaOH, wash with distilled water, and then digest for 2 hours at 100°C in 3M HCl. Finally, wash with distilled water until neutral to pH test paper, transfer to a Pyrex tray, and dry at 100°C.

COLUMN PREPARATION

Pretreatment Column: Add 2 ml of water to the column, with the stopcock closed; then add 20 ml of a 1:1 slurry of charcoal. Drain all except 2 ml of water, then add 2 ml of a 1:1 slurry of 100 to 200 mesh Dowex 50 W-X8. When the resin has settled, but the water is not completely drained, add a 2-cm thick layer of sand.

Separation Column: Add 2 ml of water to a column, with the stopcock closed. Add 20 ml of a 1:1 slurry of Dowex 1-X8 (100 to 200 mesh). Twirl the tube before the water drains to the level the resin surface. Add 2 cm of sand before all the water drains from the column. Convert the resin to the hydroxide form by adding 150 ml of 3M NaOH. Wash with water until the effluent is neutral to pH test paper.

ANALYTICAL PROCEDURE

1. Collect urine samples in vessels containing 5 ml of 20-50 mesh Dowex 50 W-X8 per 100 ml of urine.
2. Dilute 25 ml of the preserved urine to 250 ml.
3. Pass 50 ml of diluted urine through the pretreatment column, and discard the effluent.
4. Pass the remaining 200 ml of diluted urine through the column, and collect the effluent in a polyethylene bottle.
5. Pass 100 ml of the clarified urine through each of two Dowex 1-X8 columns.
6. Rinse the columns with 50 ml of distilled water, and allow them to stand overnight. Do not drain; let approximately 2 ml of water remain on top of the resin.
7. Flush the water from the columns with 10 ml of 0.3M NaOH. Discard.
8. Elute the fluoride with five 25-ml portions of 0.3M NaOH; collect each 25-ml fraction in a colorimeter tube.
9. Prepare standards of 0 to 25 $\mu\text{g F}^-$ in 25 ml of 0.3M NaOH.
10. To each standard and fraction collected, add 5 ml of mixed color reagent.
11. Read absorbance at 536 nm versus the reference solution.

CALCULATIONS

1. Plot absorbance versus $\mu\text{g F}^-$ for the standards, and determine the content of each fraction.
2. Add the concentrations of fluoride in all 10 fractions for each sample.
3. The total fluoride in the fractions is the amount per 25 ml of urine.
4. The $\mu\text{g/liter} = \text{fraction total} \times 40$.

REFERENCES

1. N.A. Talvitie and L.W. Brewer, "Separation of Fluoride by Ion Exchange: Application to Urine Analysis," Am Ind Hyg Assoc J 2(2):287 (1960).

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INDUCTIVELY-COUPLED PLASMA SPECTROSCOPY

ABSTRACT

Inductively-coupled plasma (ICP) spectroscopy is an atomic emission technique which can quantitatively identify elements in the PPM to PPB range. The liquid sample is converted into a fine aerosol which is carried by an argon stream into a high-temperature plasma. The plasma desolvates the droplets and dissociates the sample into individual excited atoms and ions which emit light at wavelengths characteristic of the elements present. The intensity is directly proportional to the concentration of the element present in the sample. The technique is comparable to atomic absorption (AA) in many respects, but can generally be used for analysis of a wider range of elements.

APPLICATIONS AND LIMITATIONS

The ICP has several advantages when compared with atomic absorption techniques, including the following:

1. The programmable grating allows the rapid analysis of multiple elements, whereas AA is limited to one element per lamp.
2. The detection limits are generally better than those of flame AA but less than graphite furnace AA. The detection limits for most elements are given in Table B-5.
3. The high linear dynamic range, often 4-5 orders of magnitude, permits the determination of major, minor, and trace elements without dilution of the sample. The maximum linear range values for certain elements are listed in Table B-5.
4. The high temperature of the plasma allows the determination of refractory elements, such as P, B, W, Zr, and U.
5. Use of the plasma reduces chemical matrix effects. For example, refractories and metal oxides seldom form in the plasma. In addition, the presence of easily oxidized elements, such as alkalis, is less likely to affect the signal level than in AA.

There are several limitations to the use of ICP. Actual method detection limits are matrix dependent and may vary with the sample. It is important to run reagent blanks for each batch of samples to correct for contaminants and to run interference samples to determine interelement correction factors for each element. Because of the sensitivity of the technique, it is best to use ultra-high purity grade reagents or redistilled acids. Finally, the most sensitive wavelength is not necessarily the appropriate one to use. Depending upon the interferences present or the concentration of the analyte, it may be necessary or desirable to select an alternate, less sensitive wavelength for the analysis.

ES&H NOTES

Some of the metals determined by ICP are designated as carcinogens by the ACGIH and by the IARC. These materials should be handled in a Designated Area, typically a laboratory hood, to minimize respiratory exposure. The room and/or hood shall be clearly labeled with a sign indicating that a carcinogen is in use.

Because hydrofluoric acid is highly toxic and corrosive, avoid inhalation, ingestion, or contact. Wear appropriate gloves and handle in a hood. Wash skin after use to avoid potential tissue damage.

APPARATUS

Inductively Coupled Plasma Spectrometer, Perkin-Elmer Model ICP/6500

Peristaltic pump

Assorted laboratory equipment such as glassware and plasticware, hot plates, and pipettes

REAGENTS

See "General Procedures for Atomic Absorption Spectroscopy," Section B of this Manual, for a list of appropriate reagents.

SAMPLE PREPARATION

Sample preparation is identical to that listed in "General Procedures for Atomic Absorption Spectroscopy," Section B of this Manual.

ANALYTICAL PROCEDURE

1. Turn on the power to the ICP, the RF generator, the computer, and the printer. Turn on the water and argon supplies.
2. Set up the instrument as indicated in the Instruction Manual, Reference 3.
3. Select appropriate wavelengths and conditions using the Methods Development Manual (Reference 4) or Table B-5.
4. Aspirate a series of standards and samples, following the instructions on the computer terminal. The computer program will calculate the calibration curve and the elemental concentrations in the samples.

QUALITY ASSURANCE

Good quality control procedures encourage the use of the following standards and check samples (Reference 9):

1. Calibration blank - used to establish the analytical curve and to flush the system between samples. Dilute 2 ml of 1:1 HNO₃ plus 10 ml of 1:1 HCl to 100 ml with distilled water.
2. Reagent blank - used to correct for contaminants in the reagents. Carry all reagents used in the sample preparation, in the same volumes as the samples, through the entire procedure.
3. Instrument check standard - a multi-element standard of known concentration, used to verify instrument drift. The concentrations used should equal the midpoint of the respective calibration curves.
4. Interference check sample - a standard containing both interfering and analyte elements in known concentrations, used to determine interelement correction factors. Spike a known sample with 100 µg/L or 5 times the detection limit of anticipated interferences.
5. QA control sample - used to verify calibration standards. Obtain from an outside source a standard at a concentration near 1 PPM in the same acid matrix as the calibration standard. The analyzed result should be $\pm 5\%$ of the true value.

REFERENCES

1. P.W.J.M. Boumans, Line Coincidence Tables for Inductively Coupled Plasma Atomic Emission Spectrometry (New York: Pergamon Press, 1980).
2. M.L. Parsons, A. Foster, and D. Anderson, An Atlas of Spectral Interferences in ICP Spectroscopy (New York: Plenum Press, 1980).
3. Instructions for ICP/6500 Inductively Coupled Plasma System, Publication No. 0993-8131 (Norwalk, CT: The Perkin-Elmer Corp., 1984).
4. G.F. Wallace and P. Barrett, Analytical Methods Development for Inductively Coupled Plasma Spectrometry, Publication No. 0993-9609 (Norwalk, CT: The Perkin-Elmer Corp., 1981).
5. T. Hayakawa, F. Kikui, and S. Ikeda, "The Determination of I, P, B, S, As and Sn by Inductively Coupled Plasma Emission Spectroscopy Using Lines at Vacuum Ultra-Violet Wavelengths," Spectrochim Acta 37B(12):1069 (1982).
6. D.D. Nygaard and D.A. Leighty, "Inductively Coupled Plasma Emission Lines in the Vacuum Ultraviolet," Appl Spectrosc 39(6):968 (1985).
7. ICP Spectrometry: Instrumentation and Operating Parameters, Publication No. ICP-252-08-MK-E (Sunland, CA: Bausch & Lomb/Applied Research Laboratories).
8. Unpublished data (Metuchen, NJ: Jobin-Yvon/Instruments SA).
9. The Federal Register, Part V: Environmental Protection Agency 49(209):43433 (Oct. 26, 1984).

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TABLE B-5
ICP PARAMETERS

ELEMENT	(a) MOST SENSITIVE ANALYTICAL WAVELENGTH (nm)	(a) DETECTION LIMIT ($\mu\text{g/ml}$)	(b) MAXIMUM LINEARITY ($\mu\text{g/ml}$)	INTERFERENCES(c)
Ag	328.07	.005		
Al	309.28(Doublet)	.02	100	Large Mg, Fe
As	193.70 189.04 (d)	.04 .01	500	Al $\approx$ 10 PPM; C peak present in normal Ar
Au	242.80	.01		
B	249.77(Doublet) 182.64 (d)	.003 .006	200	Fe $\approx$ 2 PPM; second B line nearby
Ba	455.40	.0009		
Be	313.04	.0002		
Bi	223.06	.02		
C	193.09	.03		Occurs in all standard Argon
Ca	393.37	.0001		
Cd	214.44	.002	200	
Ce	413.76	.04		
Co	238.89	.004	100	
Cr	205.55	.004	500	
Cs	894.36 (e)			
Cu	324.75	.004	200	

ELEMENT	(a) MOST SENSITIVE ANALYTICAL WAVELENGTH (nm)	(a) DETECTION LIMIT ($\mu\text{g/ml}$)	(b) MAXIMUM LINEARITY ($\mu\text{g/ml}$)	INTERFERENCES (c)
Dy	353.17	.007		
Er	337.27	.007		
Eu	381.97	.002		
Fe	238.20	.003	50	Large Co
Ga	294.36	.03		
Gd	342.25	.009		
Ge	209.43	.03		
Hf	339.98	.008		
Hg	194.23	.02		
Ho	345.60	.004		
I	178.28 (f)	.02		
Ir	230.61	.04		
Ir	224.27	.02		
K	769.90 (f)	.1		
La	333.75	.007		
Li	670.78	.002		
Lu	261.54	.0007		
Mg	279.55	.0001		

ELEMENT	(a) MOST SENSITIVE ANALYTICAL WAVELENGTH (nm)	(a) DETECTION LIMIT ($\mu\text{g/ml}$)	(b) MAXIMUM LINEARITY ($\mu\text{g/ml}$)	INTERFERENCES(c)
Mn	257.61	.0009	50	
Mo	202.03	.005	200	
Na	589.00(Doublet)	.02		Argon peak
Nb	309.42	.02		
Nd	401.22	.03		
Ni	221.65	.007	100	Large Si overlap
Os	225.58	.0002		
P	213.62 177.50 (d)	.05 .008	200	Large Cu; Fe $\equiv$ 2 PPM; Al $\equiv$ 2 PPM
Pb	220.35	.03	500	Al $\equiv$ 2 PPM; Ni $\equiv$ 2 PPM
Pd	340.46	.03		
Pr	390.84	.025		
Pt	214.42	.02		
Rb	780.02 (e)			
Re	197.31	.004		
Rh	250.43	.02		
Ru	240.27	.02		
S	180.73 (d)	.02	750	Ca $\equiv$ 5 PPM
Sb	206.83	.02		

ELEMENT	(a) MOST SENSITIVE ANALYTICAL WAVELENGTH (nm)	(a) DETECTION LIMIT ($\mu\text{g/ml}$)	(b) MAXIMUM LINEARITY ($\mu\text{g/ml}$)	INTERFERENCES(c)
	WAVELENGTH (nm)	($\mu\text{g/ml}$)	($\mu\text{g/ml}$)	
Sc	361.38	.001		
Se	196.03	.05		
Si	251.61	.008		Possible V interference (e)
Sm	359.26	.03		
Sn	189.98 (d)	.02		
Sr	407.77	.0003		
Ta	301.25	.02		
Tb	350.92	.02		
Te	214.28	.03		
Th	283.73	.04		
Ti	334.94(Doubl et)	.003	100	
Tl	190.86	.03		
Tm	313.13	.004		
U	385.96	.2	1000	Large Fe
V	309.31	.003	200	Large Al; Mg $\approx$ 5 PPM
W	207.91	.02	200	
Y	371.03	.002		
Yb	328.94	.001		

ELEMENT	(a) MOST SENSITIVE ANALYTICAL WAVELENGTH (nm)	(a) DETECTION LIMIT ($\mu\text{g/ml}$)	(b) MAXIMUM LINEARITY ($\mu\text{g/ml}$)	INTERFERENCES(c)
	WAVELENGTH (nm)	($\mu\text{g/ml}$)	($\mu\text{g/ml}$)	

Zn 213.86 .001

Zr 343.82 .005 100

- (a) Source - Reference 1
 (b) Source - Reference 4
 (c) Apparent analyte concentration due to 1000 PPM of interferent. Source - Reference 4
 (d) Purge required. Source - Reference 5
 (e) Source - Reference 8
 (f) Source - Reference 7

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TOTAL LEAD AND COPPER IN DRINKING WATER

ABSTRACT

First-draw samples of water from drinking fountains and sinks used for coffee preparation and ice from ice machines are digested with nitric acid. Total lead is quantitated using graphite furnace atomic absorption spectroscopy at 283.3 nm; total copper, using flame AA at 324.8 nm.

APPLICATIONS AND LIMITATIONS

The current action level for lead in drinking water is 15 PPB, requiring the use of graphite furnace AA for detection. Using this procedure, the detection limit for lead is .005 PPB. The higher action level for copper, 1.3 PPM, permits the use of flame AA, having a detection limit of .001 PPM. (The indicated detection limits are published values. Varying the sample preparation techniques and/or analytical conditions can improve the quantitation limits.)

APPARATUS

Polyethylene bottles, 1000 ml, standard or I-Chem Protocol C

Atomic absorption spectrophotometer - Perkin-Elmer Model 6500 with computer data acquisition, for graphite furnace analysis of lead

Graphite furnace - Perkin-Elmer Model 500

Autosampler - Perkin-Elmer Model AS-40

Recorder - Perkin-Elmer Model 56

Electrodeless discharge lamp for Lead

Atomic absorption spectrophotometer - Perkin-Elmer Model 703, for flame AA analysis of copper

Hollow cathode lamp for Copper

Beakers, 150 ml, with watchglass covers

Graduated cylinders, 25 ml

Hot plate

REAGENTS

Nitric acid, conc. (70% HNO₃), J.T. Baker Ultrex

Nitric acid, 1:1

Stock standards (1000 µg/ml) - A commercially-prepared stock standards in nitric acid are used.

Lead working standards - Prepare working standards of between 10 and 100 ng/ml. These standards will be acidified to the same strength as the stock standard using Ultrex nitric acid. **STANDARDS SHALL BE REMADE EVERY DAY.**

Copper working standards - Prepare working standards of 1, 2, and 5 µg/ml. These standards will be acidified to the same strength as the stock standard using Ultrex nitric acid.

SAMPLING PROCEDURE

1. Standard polyethylene bottles may be used for routine water analyses. For drinking water surveys, use I-Chem Protocol C bottles, which have been cleaned using an EPA protocol. Alternatively, standard sample bottles may be used after cleaning according to the EPA protocol.
2. The sample size will be 1000 ml, taken as a first draw from the water fountain, sink or ice machine after standing for at least 6 hours. Run water down the inside of the bottle to prevent splashing of the acid, leaving an air gap of approximately 1/2" from the bottom of the bottle neck. To sample an ice machine, grab ice with a disposable plastic glove; fill the sample bottle with ice; and discard the plastic glove.
3. Acidify the samples to pH<2 with 4 ml of 1:1 HNO₃, added either before or after collection.
4. Close the bottle firmly and agitate after filling. Seal and label appropriately.

ANALYTICAL PROCEDURE

1. Before digestion, a 1-ml aliquot of each sample will be screened for approximate lead content. These results will determine the volume of sample to be digested.
2. If the sample is to be split with a reference laboratory, divide it into two 500-ml samples, and reseal and relabel.

Sample preparation

1. Beakers and graduated cylinders for use with this procedure shall be either new and unused or cleaned according to the following EPA protocol:

Wash with detergent and tap water.

Rinse with 1:1 nitric acid and deionized water.

2. Place 100 ml of sample in a 150-ml beaker, and add 3 ml of conc. HNO_3 . Evaporate cautiously on a hot plate to near dryness, being sure not to boil or bake.
3. Add additional aliquots of acid until the sample is dissolved and colorless. Cool the beaker, and add 1 ml of 1:1 HNO_3 , warming slightly to dissolve any precipitate.
4. Transfer all remaining material to a 25-ml graduated cylinder, and dilute to volume.

Lead analysis

1. Set the autosampler programmer to the following parameters:

Sample volume - 20 μl
Number of standards - 3 or as applicable)
Last sample - as applicable
Delay time - 1 min
AA program number - 1 (or as applicable)
HGA program number - 1 (or as applicable)

4. Set the graphite furnace programmer to the following parameters:

Step 1 (Dry) - 130 °C, ramp 5 sec, hold 30 sec, gas flow 300 ml/min
Step 2 (Char) - 500 °C, ramp 5 sec, hold 20 sec, gas flow 300 ml/min
Step 3 (Atomize) - 2100 °C, ramp 0 sec, hold 5 sec, gas flow 50 ml/min, recorder -5 sec, read -2 sec
Step 4 (Cool) - 40 °C, ramp 1 sec, hold 4 sec, gas flow 300 ml/min

Store as Program #1 (or as applicable).

5. Set the Model 6500 atomic absorption spectrophotometer to the following parameters:

Wavelength - 283.3 nm
EDL power - 10 watts
Slit width - 0.7 nm Low
Signal - Peak height
Calibration read (t) - 7 sec
Mode - AA and ABS

Store as Program #1 (or as applicable).

6. Place the standards, blanks, samples, and QA samples in the autosampler. Run the samples according to the manufacturer's instructions.
7. Calculate the concentrations using the "CURVE" program on the STANDARD PAC disk for the Hewlett-Packard HP-85 calculator.

Copper analysis

1. Copper analyses of the digested sample will be run on the Model 703 flame atomic absorption spectrophotometer.
2. The procedure will be that listed in "General Procedures for Atomic Absorption Spectroscopy," Section B of this Manual.

QUALITY ASSURANCE

1. A reagent blank, consisting of at least 0.5% Ultrex nitric acid in distilled water, shall be run at the beginning of each sample set and after each high standard to check for memory effects.
2. A medium-range standard shall be rerun after every 20 samples, or at least once per sample set.
3. One sample out of 20, or at least one per sample set shall be divided prior to sample preparation and run as replicates to check precision.
4. One sample out of 20, or at least one per sample set shall be divided, one-half to be spiked at the regulatory level and run to check matrix effects on recovery and precision.
4. 10% of the samples shall be divided and run as splits with a reference laboratory.

REFERENCES

1. Analytical Methods for Furnace Atomic Absorption Spectroscopy, Publication No. 0303-0512 (Norwalk, CT: The Perkin-Elmer Corp., 1982)
2. AS-40 Auto Sampler Sequencer Version Operator's Manual, Publication No. B347-A1-M509/3.82 (West Germany: The Perkin-Elmer Corp., 1982)
3. HGA Graphics II Software Package Instructions, Publication No. NO65-0038 (Norwalk, CT: The Perkin-Elmer Corp., 1984)
4. Methods for Chemical Analysis of Water and Wastes, Publication No. EPA-600/4-79-020 (Cincinnati, OH: U.S. Environmental Protection Agency, 1983), Section 200.0 Atomic Absorption Methods for Metals, Method 239.2 Lead.

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LEAD IN URINE

ABSTRACT

Small quantities of lead in urine can be analyzed using Anodic Stripping Voltammetry (ASV). This electrochemical technique involves (1) preconcentrating the sample by forming an amalgam with a thin-film mercury electrode, and then (2) scanning the electrode potential to electrolytically dissolve the metal back into solution. The stripping current is proportional to the concentration of the analyte in the original sample. (See Reference 1 for a more complete description of the ASV technique.)

APPLICATIONS AND LIMITATIONS

Anodic Stripping Voltammetry is primarily a trace analytical technique and is not generally recommended for analyte concentrations greater than 1 PPM. Using the Metexchange reagents (Environmental Sciences Associates, Inc.), the linear range for lead in urine is 10-750 $\mu\text{g/L}$.

The presence of EDTA (used as a preservative in the sampling procedure) or Penicillamine in the samples can cause low lead recoveries. The effects of these interferences are mitigated by the addition of nickel or copper, respectively. The extreme sensitivity of the technique requires the use of high purity chemicals for all additional processing.

APPARATUS

Anodic Stripping Voltammeter, Environmental Sciences Associates (ESA) Model 3010A

Metexchange "U" Reagent Kit, from ESA, Inc., containing all the necessary reagents, standards, and equipment for the ASV analysis of lead in urine

Electrode resurfacing tool

pH Paper

Pipettes, 100 μl and 1 ml

Steel wool for cleaning the electrode

REAGENTS

Hydrochloric acid, reagent grade

ANALYTICAL PROCEDURE

Instrument preparation

1. Condition the electrode before each day's run. Remove the stirring rod, and clean the electrode, using steel wool wrapped around the resurfacing tool. Rinse with distilled water, and replace the stirring rod. Place a tube of the mercury plating solution (red dot tube from either Reagent Kit) over the electrode, and run three 1-minute analytical cycles to lay down a thin film of mercury. The plating solution can be reused several times. (For detailed instructions, see Reference 2.)
2. Adjust the parameter settings as indicated for the individual sample types.
3. Adjust the Blank Correction Dial by placing a Lo Level Control tube (blue dot tube from the Reagent Kit) on the cell head. Be sure to **rock the tube gently (do not shake)** several times before uncapping to assure that the reagent is well mixed. Record the digitally-displayed concentration, and repeat the run with a separate Control tube until 2 consecutive concentrations differ by 5 or less for urine standards, 4 or less for blood standards. Average the last 2 values, subtract the assigned Lo Level Control value (listed on the reagent box), and adjust the Blank Correction Dial for the difference.
4. Adjust the Calibration Control Dial by placing a Hi Level Control tube (green dot tube from the Reagent Kit) on the cell head. Be sure to **rock the tube gently (do not shake)** several times before uncapping to assure that the reagent is well mixed. Record the digitally-displayed concentration. Calculate the optimum dial setting using the following formula:

$$\text{Setting} = \frac{\text{Assigned control value (on box)}}{\text{Digital reading}} \times \text{Dial setting used}$$

Adjust the Calibration Control Dial, rinse the electrode with a used Lo Level control, and repeat the analysis with a second Hi Level control. Repeat the entire procedure if the second reading is not within ± 10 of the assigned value for urine, ± 5 for blood.

Urine samples

1. Set the analytical parameters to the values recommended in Reference 3.
2. Calibrate the instrument as in the "Instrument preparation" section.
3. Acidify the homogenized urine sample to pH 3-5 with reagent-grade HCl. (Use pH paper rather than a pH electrode to avoid potential contamination of the sample.) Pipette 1 ml of urine into a reagent tube supplied with the Metexchange "U" Kit, and allow 5 minutes for equilibration.
4. Place the tube on the cell head, stir the sample for 5 seconds, depress the START ANALYSIS Switch, and record the concentration when the READY light appears (150 seconds analysis time).
5. Check the validity of the calibration after 20 samples or at the end of each series.
6. At the end of the day, replace the sample tube with a previously-run Lo Level Control sample (or distilled water, if the instrument will not be used in the next few days).

REFERENCES

1. W.M. Peterson and R.V. Wong, "Fundamentals of Stripping Voltammetry," Am Lab 13(11):116 (1981).
2. Model 3010A trace Metals Analyzer Instruction Manual (Bedford, MA: Environmental Sciences Associates, Inc., 1987).
3. "Direct Analysis of Lead in Urine Using Metexchange 'U' Reagent with No Sample Pretreatment," Publication No. TMA-2, Methods Manual for ESA 3010A Anodic Stripping Voltammeter (Bedford, MA: Environmental Sciences Associates, Inc.).

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MERCURY IN URINE

ABSTRACT

Urine samples are decomposed with nitric acid, and then the mercury is reduced to the elemental state with stannous chloride. The mercury vapor is passed through an absorption cell with quartz end windows and then analyzed by atomic absorption using the 253.7 nm Hg resonance line. (See also "General Procedures for Atomic Absorption Spectroscopy," Section B of this Manual.)

APPLICATIONS AND LIMITATIONS

The sensitivity for a 1.0-ml urine sample is 3 µg/L. The range extends up to 0.3 mg/L.

Metals such as copper, gold, or platinum form alloys with mercury and thus will cause a negative response. Water vapor or organic solvents that absorb at 253.7 nm cause a positive response. Another limitation to this method is that some organic mercury compounds are not decomposed by the cold digestion technique.

APPARATUS

Atomic absorption spectrophotometer, Perkin-Elmer Model 703

High-efficiency bubbler, 100-ml size

Mercury evolution train - This consists of a rotometer covering the 0 to 5 L/min range, a high-efficiency bubbler, a midget impinger as a safety trap, a drying tube filled with magnesium perchlorate, and the absorption cell. All components are connected to an air supply line with minimum lengths of Tygon tubing.

Pipets, 1-, 2-, and 5-ml sizes

Volumetric flask, 1000 ml

REAGENTS

Nitric acid, conc. (70% HNO₃)

n-Octyl alcohol

Hydrochloric acid (6N) - Add 500 ml of conc. HCl to 500 ml of distilled water.

Stannous chloride solution, 20% (w/v) in 6N HCl - Dissolve 10 g of stannous chloride in 50 ml of 6N HCl.

Mercury stock standard (1000 $\mu\text{g Hg/ml}$) - A commercially-prepared stock standard in nitric acid is used.

Mercury working standard (1 $\mu\text{g Hg/ml}$) - Pipet 1 ml of the 1000- $\mu\text{g/ml}$ stock standard into a 1-liter volumetric flask. Add 20 ml of conc. HNO_3 , and dilute to volume with distilled water. PREPARE FRESH DAILY.

ANALYTICAL PROCEDURE

1. Transfer 2 ml of urine to a high-efficiency bubbler.
2. Add 5 ml of HNO_3 , and allow it to react at room temperature for at least 3 minutes.
3. Dilute to 50 ml with distilled water. Add 3 drops of n-octyl alcohol as a surfactant and 1 ml of stannous chloride solution, and connect the flask to the bubbler tube in the generating train.
4. Open the air valve, and pass air through the train at a rate of 2 L/min.
5. Record the detector response on the recorder.
6. Run standards of 0.001 to 1 $\mu\text{g Hg}$ in the same manner, rinsing the pipet in the solution. Different standard quantities of Hg can be added to the same standard solution since the Hg is completely removed during the reaction.

CALCULATIONS

1. Make a calibration curve by plotting peak height or area under the curve versus $\mu\text{g Hg}$ on semilog graph paper.
2. From the calibration curve, read $\mu\text{g Hg}$ for each of the samples.
3.
$$\text{Hg concentration } (\mu\text{g/ml}) = \frac{\mu\text{g Hg found}}{\text{ml sample taken}}$$
4. Alternatively, the concentration may be calculated using the "CURVE" program on the STANDARD PAC disk for the Hewlett-Packard HP-85 calculator.

REFERENCES

1. W.R. Hatch and W.L. Ott, "Determination of Sub-Microgram Quantities of Mercury by Atomic Absorption Spectrophotometry," Anal Chem 40:2085 (1968).
2. "Determination of Mercury in Urine," Methods of Air Sampling and Analysis, ed J.P. Lodge, Jr. (3rd ed; Chelsea, MI: Lewis Publishers, 1989), Method 815.

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NITROGEN DIOXIDE IN AIR

ABSTRACT

Nitrogen dioxide is collected in sulfanilic acid. The diazotized NO_2 is coupled with N-(1-naphthyl)-ethylenediamine, forming a red-violet azo dye. The dye color is read at 550 nm.

APPLICATIONS AND LIMITATIONS

The analytical range of this method is 0.005 to 5 PPM by volume or 0.01 to 10 $\mu\text{g/L}$ when sampling with fritted bubblers. For greater accuracy, standardize using accurately-known gas samples rather than the more convenient nitrite solution.

The main limitations are due to interferences from larger concentrations of strong oxidizing and reducing agents, such as sulfur dioxide, hydrogen peroxide, ozone, and chlorine. Many of these interferences can be mitigated by the use of various chemical agents (see Reference 1) or by measuring the absorbance within 1 hour of sample collection.

APPARATUS

Spectrophotometer, Hewlett-Packard Model 8450A

Bubbler, all-glass

Grab-sample bottles, 30- to 500-ml sizes

Assorted laboratory glassware

REAGENTS

Sulfanilic acid, anhydrous

Acetic acid, glacial

N-(1-naphthyl)-ethylenediamine dihydrochloride (0.1%) - Dissolve 0.1 g of the salt in 100 ml of distilled water. When stored in the refrigerator in a well-stoppered amber bottle, this reagent is stable for several months.

Absorbing reagent - Dissolve 5 g of sulfanilic acid in almost 1 liter of distilled water containing 140 ml of glacial acetic acid. Add 20 ml of a 0.1% solution of N-(1-naphthyl)-ethylenediamine dihydrochloride, and dilute to 1 liter. When stored in a brown bottle in the refrigerator, the reagent is stable for several months. Allow it to warm to room temperature before using.

Sodium nitrite stock standard (0.0203 mg NaNO_2 /ml) - Add 2.030 g of sodium nitrite to 1 liter of distilled water. This solution is stable for 90 days at room temperature and for 1 year when refrigerated in a brown bottle.

Sodium nitrite working standard (Equivalent to 10 μl NO_2 /ml) - Prepare fresh by diluting 1 ml of stock sodium nitrite solution to 100 ml. This solution of 0.0203 g of NaNO_2 per liter is such that 1 ml of this working standard, added to the absorbing reagent, produces a color equivalent to that of 10 μl of NO_2 or 10 PPM of NO_2 in 1 liter of air at STP.

ANALYTICAL PROCEDURE

For less than 1 PPM of NO_2 :

1. Place 10 ml of absorbing reagent in a fritted-glass bubbler.
2. Collect the sample at a 0.4-L/min rate for about 10 minutes or until sufficient red-violet color has developed.
3. Allow the color to develop for 15 minutes, transfer the sample to a cuvette, and read at 550 nm in the spectrophotometer. Use unexposed absorbing reagent to set instrument at zero absorbance.

For more than 1 PPM of NO_2 :

1. Collect sample in an evacuated 250-ml or larger bottle containing 10 ml of absorbing reagent. Shake the sample after collecting. Let set for 15 minutes.
2. Read at 550 nm after transferring the liquid containing the NO_2 to a cuvette.

CALIBRATION

1. To eight 25-ml volumetric flasks, add 0.05, 0.10, 0.20, 0.30, 0.40, 0.50, 0.60, and 0.70 ml of the working nitrite solution.
2. Dilute to 25 ml with absorbing reagent and mix.
3. Allow the color to develop for 15 minutes, and then read at 550 nm against a zero of absorbing reagent.

4. Plot the absorbances of the standards versus μl of nitrogen dioxide per ml of absorbing reagent. The latter values are equal to the corresponding ml of working nitrite solution times 0.4.* The plot follows Beer's Law. Through the origin draw a straight line giving the best fit, and determine the slope, K, which is μl of NO_2 intercepted at an absorbance of exactly 1. For 1-cm cells, the value of $K \approx 0.73$.

CALCULATIONS

Compute the concentration of nitrogen dioxide in the sample using the following equation:

$$\text{PPM NO}_2 = AK/V$$

where

A = absorbance

K = slope of calibration curve

V = volume of air sampled in liters/ml absorbing reagent

REFERENCES

1. B.E. Saltzman, "Colorimetric Microdetermination of Nitrogen Dioxide in the Atmosphere," Anal Chem 26:1949 (1954).
2. B.E. Saltzman, "Determination of Nitrogen Dioxide and Nitric Oxide: Saltzman Method," Selected Methods for the Measurement of Air Pollutants, Publication No. 999-AP-11 (Cincinnati, OH: U.S. Public Health Service, 1965), p. C-1.
3. "Determination of Nitrogen Dioxide Content of the Atmosphere (Griess-Saltzman Reaction)," Methods of Air Sampling and Analysis, ed J.P. Lodge, Jr. (3rd ed; Chelsea, MI: Lewis Publishers, 1989), Method 406.

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* The molar volume at standard conditions of 760 mm Hg and 25°C is 24.47 liters. One mole of nitrogen dioxide and 0.72 mole of sodium nitrite produce the same color. Since 1 ml of the working solution contains 2.03×10^{-5} g of NaNO_2 (molecular weight = 69), then

$$\frac{2.03 \times 10^{-5}}{69} \times \frac{24.47}{0.72} = 10^{-5} \text{ liters of NO}_2 \text{ or } 10 \mu\text{l}.$$

Therefore 1 ml of nitrite solution (10 μl NO_2) per 25-ml volume is equivalent to 10/25 or 0.4 μl of NO_2 per ml.

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OZONE IN AIR

(Colorimetric Method)

ABSTRACT

Air is drawn through a midget impinger containing 10 ml of neutral potassium iodide solution. The ozone liberates iodine, which is determined colorimetrically at 352 nm.

APPLICATIONS AND LIMITATIONS

This method is simple and rapid. The analytical range extends from 0.01 to 10 PPM. The sensitivity of the method is dependent on the volume of air sampled, and the analysis must be completed within 1 hour after sampling.

Main interferences are reducing compounds, such as sulfur dioxide, nitric oxide, and hydrogen sulfide. Some oxidants, such as halogens and hydrogen peroxide, will also interfere.

An alternative, non-instrumental technique uses titration of the liberated iodine using sodium thiosulfate (see "Ozone in Air (Titration Method," Section B of this Manual).

APPARATUS

Spectrophotometer, Hewlett-Packard Model 8450A

Midget impinger, all-glass

Assorted laboratory glassware

REAGENTS

Potassium dihydrogen phosphate

Disodium hydrogen phosphate, anhydrous

Potassium iodide

Absorbing reagent (1% KI) - Dissolve 13.61 g of potassium dihydrogen phosphate, 14.2 g of anhydrous disodium hydrogen phosphate, and 10 g of potassium iodide, in that order, in 1 liter of distilled water. Keep at room temperature for at least 1 day before using. Store in a brown bottle in a refrigerator. PREPARE MONTHLY.

Iodine, resublimed

Iodine stock standard (0.025M I₂) - Dissolve successively 16 g of KI and 3.1730 g of iodine in 500 ml of distilled water. Keep at room temperature for at least 1 day before using. Standardize with 0.10N sodium thiosulfate shortly before use.

Iodine working standard (0.00125M I₂) - Pipet 5 ml of stock solution into a 100-ml volumetric flask, and dilute to the mark with the absorbing reagent.

ANALYTICAL PROCEDURE

1. Pipet 10 ml of absorbing reagent in the midget impinger.
2. After receiving the samples, measure the volume, and transfer to a clean cuvette. Do not dilute with rinse water!
3. Determine the absorbance of the yellow iodine solution at 352 nm, using distilled water as the reference. Also determine the absorbance of a reagent blank.
4. Run a series of standards through Steps 2 and 3 by pipetting 0.2-, 0.4-, 0.6-, and 0.8-ml portions of the working solution (0.1, 0.2, 0.3, and 0.4 μ moles I₂/10 ml of absorbing reagent) in separate 25-ml volumetric flasks. Dilute to the mark with absorbing reagent, mix well, and read the absorbance of each at 352 nm.
5. Plot absorbance (after subtracting the absorbance of a reagent blank) versus molar concentration in μ moles/10 ml.

CALCULATIONS

Since 1 mole of ozone liberates 1 mole of iodine, one can read μ moles of ozone directly from the calibration curve, if the total sample volume is 10 ml. If the sample was diluted prior to analysis, the proper dilution factor must be included in the calculation.

$$\text{PPM ozone} = \frac{\mu\text{moles ozone} \times 24.47 \text{ liters/mole}}{\text{Volume of air sampled in liters at STP}}$$

REFERENCES

1. "Determination of Oxidizing Substances in the Atmosphere," Methods of Air Sampling and Analysis, ed J.P. Lodge, Jr. (3rd ed; Chelsea, MI: Lewis Publishers, 1989), Method 411.

2. B.E. Saltzman, "Determination of Oxidants (Including Ozone: Neutral Buffered-Potassium Iodide Method," Selected Methods for the Measurement of Air Pollutants, Publication No. 999-AP-11 (Cincinnati, OH: U.S. Public Health Service, 1965), p. D-1.

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OZONE IN AIR

(Titration Method)

ABSTRACT

Ozone is collected in KI solution; and the iodine liberated is titrated with sodium thiosulfate, using starch as an indicator.

APPLICATIONS AND LIMITATIONS

This method is a rapid and simple alternative to the colorimetric technique (see "Ozone in Air (Colorimetric Method)," Section B of this Manual) and uses no expensive equipment. The sensitivity is dependent on the volume of air sampled, making the technique especially good for larger concentrations of ozone.

The main limitation is that the liberated iodine is very sensitive to reducing vapors or dusts such as SO_2 or H_2S . Also, strong oxidants, such as halogens, peroxides, etc., will liberate iodine.

ES&H NOTES

Chromates are designated as Class A1 carcinogens by the ACGIH and Class 1 carcinogens by the IARC. Potassium dichromate should be handled in a Designated Area, typically a laboratory hood. The room and/or hood shall be clearly labeled with a sign indicating that a carcinogen is in use.

APPARATUS

Buret, 5-ml capacity

Magnetic stirrer, with Teflon-covered bar magnet

Midget bubbler, all-glass

REAGENTS

Potassium iodide

Potassium iodide solution (5%) - PREPARE FRESH DAILY.

Starch indicator solution - Dissolve 1 g of soluble starch in 100 ml of boiling distilled water.

Hydrochloric acid, 1:1 in distilled water

Potassium dichromate solution (0.1N) - Dissolve 4.904 g of $K_2Cr_2O_7$ (dried for 2 hours at $130^{\circ}C$) in 1 liter of water.

Sodium bicarbonate

Sodium thiosulfate solution (0.01N) - Dissolve 2.5 g of $Na_2S_2O_3 \cdot 5H_2O$ in 1 liter of distilled water. Standardize against $K_2Cr_2O_7$ by the following method: Dissolve 5 g of KI and 4 g of $NaHCO_3$ in 300 ml of H_2O . Slowly add 1:1 HCl until no more CO_2 is released; then add a 10-ml excess. Add 35 ml of 0.1N $K_2Cr_2O_7$, and mix thoroughly. Add a stirring bar, and place on a magnetic stirrer. Titrate the stirred solution with thiosulfate to a light straw yellow. Add 1 ml of starch indicator, and titrate until the blue is replaced with the pale green color of $CrCl_3$. From the volume of thiosulfate used, calculate the normality.

ANALYTICAL PROCEDURE

1. Collect samples in 10 ml of freshly prepared KI.
2. Transfer the collecting solution to an Erlenmeyer flask, add a Teflon stirring bar, and place on a magnetic stirrer.
3. Add 1 ml of 1:1 HCl and 1 ml of starch indicator.
4. Titrate with standard thiosulfate to the colorless end point.

CALCULATIONS

1 ml 0.01N $Na_2S_2O_3$ = 0.24 mg ozone

REFERENCES

1. D.H. Beyers and B.E. Saltzman, "Determination of Ozone in Air by Neutral and Alkaline Iodide Procedures," Am Ind Hyg Assoc J 19:251 (1958).

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SULFUR DIOXIDE IN AIR

ABSTRACT

Sulfur dioxide is collected in a midget impinger containing hydrogen peroxide, which converts the SO_2 to sulfuric acid. The quantity of sulfuric acid absorbed is determined by ion chromatography.

APPLICATIONS AND LIMITATIONS

The quantitative detection limit for the method is 0.017 mg/m^3 for a 60 L air sample. The limit of quantitation is 0.042 mg/m^3 with a relative standard deviation of less than 0.10.

Particulate sulfate compounds and sulfuric acid will interfere with the analysis but can be removed by use of a prefilter. Sulfur trioxide gas will also give a positive interference.

APPARATUS

Midget impinger, fritted glass

Ion chromatograph, Dionex Model 2110i with electrolytic conductivity detector

Integrator, Hewlett-Packard Model 3390A or 3396A

Syringes, liquid, 5 cc, plastic

REAGENTS

Hydrogen peroxide (0.3N) - Dilute 17 ml of 30% H_2O_2 to 1 liter with distilled water.

Eluent solution, 0.0029M NaHCO_3 /0.0023M Na_2CO_3 - Dissolve $0.9744 \pm 0.0005 \text{ g}$ of NaHCO_3 and $0.9752 \pm 0.0005 \text{ g}$ of Na_2CO_3 in 4 liters of distilled water.

Regenerant solution, 0.025N H_2SO_4 - Dilute 2.8 ml of concentrated H_2SO_4 to 4 liters with distilled water.

Sulfate stock standard (1000 $\mu\text{g/ml SO}_4^{2-}$) - Dissolve and dilute 1.4792 g of Na_2SO_4 to 1 liter with distilled water.

Sulfate working standards - Prepare standards in the range of 1-100 $\mu\text{g/ml}$. PREPARE FRESH MONTHLY, OR WEEKLY IF BELOW 50 $\mu\text{g/ml}$.

ANALYTICAL PROCEDURE

1. Collect the sample in a midget impinger containing 15 ml of 0.3N hydrogen peroxide.
2. Measure and record the total volume of each sample before analysis.
3. Set up the ion chromatograph and run the samples and standards as described in "Common Anions in Aqueous Solutions," Section B of this Manual. The retention time for the sulfate anion will be approximately 18 minutes at a flow rate of 138 ml/hr.

CALCULATIONS

1. Calculate a calibration factor for the sulfate anion:
$$CF = \text{Peak area for standard} / \mu\text{g sulfate in standard}$$
2. Calculate the sulfate concentration for the samples:
$$\mu\text{g Sulfate} = \text{Peak area for sample} \times CF$$
3. Convert sulfate concentration to SO_2 concentration:
$$\mu\text{g SO}_2 = (\mu\text{g SO}_4^{2-}) \times (0.667) \times (\text{Total sample volume})$$

where 0.667 is the gravimetric ratio of $\text{SO}_2/\text{SO}_4^{2-}$.

REFERENCES

1. "Sulfur Dioxide in Workplace Atmospheres (Impinger)," OSHA Analytical Methods Manual (Salt Lake City, UT: Occupational Safety and Health Administration, 1985), Method ID-104.
2. "Determination of Sulfur Dioxide Content of the Atmosphere (Hydrogen Peroxide Method)," Methods of Air Sampling and Analysis, ed J. P. Lodge, Jr. (3rd ed; Chelsea, MI: Lewis Publishers, 1989), Method 704C.

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THALLIUM IN URINE

ABSTRACT

Urine samples are diluted with a matrix modifier and analyzed at 276.8 nm using graphite furnace atomic absorption spectroscopy. (See also "General Procedures for Atomic Absorption Spectroscopy," Section B of this Manual.)

APPLICATIONS AND LIMITATIONS

This technique allows the direct determination of thallium in urine, avoiding time-consuming extraction techniques and the use of organic solvents. With background correction, a detection limit of 0.5 ng/ml can be achieved. Precision is 15% at 6 ng/ml. The AA sensitivity (amount of material giving an absorbance of 0.0044) is calculated to be 35 pg.

APPARATUS

Atomic absorption spectrophotometer - Perkin-Elmer Model 6500

Graphite furnace - Perkin-Elmer Model HGA 500

Autosampler - Perkin-Elmer Model AS-40

Recorder - Perkin-Elmer Model 56

Electrodeless discharge lamp for Thallium

Centrifuge tubes, 40-ml plastic

REAGENTS

Magnesium nitrate hexahydrate ($\text{MgNO}_3 \cdot 6\text{H}_2\text{O}$)

Nitric acid, conc. (70% HNO_3)

Titon X-100, scintillation grade

Matrix modifier - Dilute 1.0 g $\text{MgNO}_3 \cdot 6\text{H}_2\text{O}$, 4.0 ml conc. HNO_3 , and 0.01 ml Triton X-100 to 100 ml with distilled water.

Hydrochloric acid (4N) - Add 333 ml of conc. HCl to 667 ml of distilled water.

Thallium stock standard (1000 µg Tl/ml) - Available commercially, or prepare by dissolving 1.1174 g of thallic oxide in 1 liter of 4N HCl.

Thallium working standard (1 µg Tl/ml) - Dilute 100 µl of 1000-µg/ml stock standard to 100 ml with distilled water.

Pooled urine sample

Thallium stock standard in urine (20 ng Tl/ml) - Dilute 0.2 ml of 1-µg/ml working standard to 10 ml with pooled urine.

Thallium working standard in urine (10 ng Tl/ml) - Dilute 1 ml of 20-ng/ml stock urine standard with 1 ml of matrix modifier.

ANALYTICAL PROCEDURE

1. Set up the autosampler and spectrophotometer as described in "Total Lead and Copper in Drinking Water Fountains," Section B of this Manual, with the following differences:

Wavelength - 276.8 nm
EDL power - 7 watts

2. Set the graphite furnace programmer to the following parameters:

Step 1 (Dry) - 180 °C, ramp 5 sec, hold 30 sec, gas flow 300 ml/min

Step 2 (Char) - 650 °C, ramp 5 sec, hold 20 sec, gas flow 300 ml/min

Step 3 (Atomize) - 2000 °C, ramp 0 sec, hold 5 sec, gas flow 5 ml/min

Step 4 (Cool) - 20 °C, ramp 1 sec, hold 4 sec, gas flow 300 ml/min

3. Combine 1 ml of sample urine and 1 ml of matrix modifier in a 40-ml centrifuge tube. Agitate to mix.
4. Place the standards, blanks, samples, and QA samples in the autosampler. Run the samples according to the manufacturer's instructions.
4. Calculate the concentrations using the "CURVE" program on the STANDARD PAC disk for the Hewlett-Packard HP-85 calculator.

REFERENCES

1. D.C. Paschal and G.G. Bailey, "Determination of Thallium in Urine with Zeeman Effect Graphite Furnace Atomic Absorption," J Anal Toxicology 10 (Nov/Dec):252 (1986).

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SECTION C

ORGANIC METHODS

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COMPOSITION OF COMMERCIAL AND PROPRIETARY PRODUCTS

ABSTRACT

A certain percentage of the laboratory workload is analysis of commercial or proprietary products to determine potential toxic hazards. The chemist may be asked to determine the composition of a solvent free from solids, or he may be given a resin solution or a paint and asked to determine the solvent in which the solid material is dissolved or suspended.

Through his experience and academic training, an analytical chemist has usually gathered a large mental file of information useful in recognizing a compound's characteristics and in evaluating those characteristics. The actual analysis of an unknown almost invariably proceeds on the basis of these value judgments via well-known schemes toward qualitative and quantitative determination of composition.

THE ANALYSIS PROCESS

Gathering Initial Observations

Many times the major component of a product can be assumed or inferred from one or more of the following easily gathered sources of information:

1. Name: Usually a trade name, but sometimes it gives a helpful hint toward the major component.

Example: Tellurac (R. T. Vanderbilt Co.) is an organic salt of tellurium.

Liqui-Moly (Lockrey Co.) is a molybdenum sulfide lubricant.

Thiofact (National Aniline Div., Allied Chemical Corp.) is a sulfur-containing indigo pigment.

2. Source: Sometimes useful in characterizing chemical class.

Example: Shell Chemical Co. is famous for petrochemicals; thus, a Shell product is most likely an organic chemical and amenable to infrared and/or gas chromatographic analysis.

Pennsylvania Glass Sand Corp. products would almost certainly contain silica as a major ingredient.

Thiokol Chemical Corp. is famous for its polysulfide-based rubber formulations.

3. Use: Often very helpful in determining chemical class.

Example: Typewriter roller cleaners are used to dissolve inks, so they are usually low-boiling-point organic solvents or solvent mixtures.

Gunpowder solvents almost always contain nitrobenzene or some other nitro product.

Bactericides and algicides for water treatment often contain quaternary ammonium salts amenable to infrared analysis.

4. Physical characteristics: Usually very helpful but possibly misleading. Practically all industrial products are secret formulations purposely doctored in some way to disguise the major constituents and active ingredients.

- a. Physical state is the most easily noted physical characteristic and one of the most difficult to mask. It must be remembered, however, that an emulsifying, wetting, or gelling agent can alter the physical state from an immiscible to a miscible liquid, from a suspension to a colloid, or from a liquid to a solid.
- b. Color is only rarely helpful. Most manufacturers use coloring agents as disguises only too successfully. The very distinctive fluorescent green of fluorescein is evident in a multitude of products from household liquid detergents to industrial leak detectors. In none of these products is fluorescein of any functional use whatsoever.
- c. Smell can often lead to an immediate value judgment for the major component. A sulfur-containing material often smells like H_2S (rotten eggs) or SO_2 (burnt matches). Amines smell fishy; esters and higher ketones, fruity; aldehydes, musty.
- d. Other physical characteristics such as density, melting and boiling points, and index of refraction should not be determined at this point unless a specific compound is already highly suspect.

5. Chemical characteristics: These are the most significant properties, yielding the most useful data. The single most important consideration when analyzing a commercial product for its constituents is to approach it step by step, proceeding from the simple to the more complex tests in a meaningful fashion. Many such schemes appear in the literature for both inorganic and organic qualitative analysis.
- a. Reaction in a Bunsen-burner flame: If a product burns completely, boils away, smokes, or chars in a flame, it is at least partially organic. If it leaves a residue or ash, it is at least partially inorganic. The color of the flame above the sample often indicates which alkali metal is present.
  - b. Solubility: Although this is, strictly speaking, a physical characteristic, it is a most helpful indicator of chemical composition. Try water, alcohol, and petroleum ether as "indicator" solvents. If the product is soluble or partially soluble in water, determine the pH; then make the solution acidic and then basic, and observe for precipitation, gas evolution, or change in color.
  - c. Reducing ability: Using one portion of the acidified solution from Step (b), add 1 drop of 1% KMnO_4 to test for reducing agents.
  - d. Oxidizing ability: To another portion of the acidified solution from Step (b) above, add 5 drops of a 10% KI - starch solution to test for oxidizing agents.
  - e. Metals content: Use atomic absorption or inductively coupled plasma (ICP) spectroscopy to determine metals in a solution.
  - f. Liquid purity and quantitation: Use the gas chromatograph to determine the number of components in an organic liquid. The resulting gas chromatogram not only indicates the number of low-to-medium boiling fractions quickly and accurately, but also can be saved for future quantitation. Note also the shape of the peak -- a long "tail" can indicate a polar or nonpolar compound, depending upon the column used.
  - g. Water content: Add a pinch of anhydrous copper sulfate, shake, and observe the color. If water is present, the white anhydride turns blue. Of course, all water solutions react in this way, but so will water in minor amounts in organic mixtures. This test is most helpful in determining amenability to later infrared analysis using NaCl windows.

6. Solvents: Since a substantial percentage of most commercial products is the solvent, a detailed discussion is presented here. Solvents vary widely; but, in general, the following rules hold:
- a. The lower molecular weight alcohols, ketones, and esters are soluble, to varying degrees, in water. All of these except methanol, ethylene glycol, and glycerine can be separated by saturating the water solution with NaOH or NaCl.
  - b. The water-insoluble alcohols, esters, ketones, ethers, and unsaturated hydrocarbons are soluble in 80% H_2SO_4 (80 ml of conc. H_2SO_4 diluted to 100 ml with water). An 80:20 mixture of H_2SO_4 and H_3PO_4 gives essentially the same solubility. Dilution of the acid layer to 3 or 4 times the original volume, followed by addition of Na_2SO_4 , causes all of these except the unsaturated hydrocarbons to come out of solution with either reagent. The H_3PO_4 lessens hydrolysis of esters.
  - c. Aromatic hydrocarbons are almost insoluble in 80% H_2SO_4 , but the solubility increases with the number of alkyl groups. Aliphatic hydrocarbons and halogenated aliphatic hydrocarbons are insoluble in 80% H_2SO_4 . Trichloroethylene and perchloroethylene, even though they are double bonded, are not soluble in 80% H_2SO_4 .
  - d. Aromatic hydrocarbons and halogenated aromatic hydrocarbons are soluble in fuming H_2SO_4 (30-33% free SO_3).
  - e. The aliphatic hydrocarbons and halogenated aliphatic hydrocarbons are insoluble in fuming H_2SO_4 , unless they are highly branched. Trichloroethylene and perchloroethylene are slowly soluble in fuming H_2SO_4 .
  - f. The refractive intercept, calculated by subtracting one-half of the specific gravity from the refractive index, gives an indication of the type of hydrocarbon present. The value of the refractive intercept is about 1.0640 for all common aromatic hydrocarbons and 1.0460 for all chain aliphatic hydrocarbons. The cyclic aliphatic hydrocarbons have a refractive intercept close to 1.0400.
  - g. A low refractive intercept indicates a greater specific gravity compared to the refractive index. This value cannot be used to identify types of solvents other than hydrocarbons, since the value varies for each alcohol, ketone, ester, and halogenated hydrocarbon.

- h. The dispersion gives an indication of the presence of aromatic hydrocarbons. The Z value on the scale of the Abbe refractometer (manufactured by Bausch & Lomb) is about 23 or 24 for aromatic hydrocarbons, whereas other solvents usually give 17, 18, or 19. On the Zeiss Abbe-type refractometer, the aromatic hydrocarbons give a reading of about 35; and other solvents, a reading of about 41.
- i. Aromatic hydrocarbons have a specific gravity close to 0.87 and a refractive index close to 1.50.

Analysis

When steam distillation is necessary, the water and solvent layers are separated. The cerate test for alcohols (described later) is run on the water layer. If this test is positive and methanol is thought to be present, test the layer for methanol, as described later under "Test for Methanol."

Any other components usually found in solvents can be separated from the water layer by saturating the water with NaOH or NaCl.

Add any solvent recovered from the water layer to the solvent layer, and dry the solvent thoroughly by adding anhydrous Na_2SO_4 . Allow the solvent to stand overnight. Drying is necessary, since many solvents form azeotropes with water. Alternatively, the water which distills over may be soluble in some of the components, thereby changing the constants.

Solvents which do not require steam distillation are also dried over anhydrous Na_2SO_4 .

Distill 100 ml or more of the dry solvents through a good fractionating column. Keep a record of the temperatures at which the solvent starts to come over and at which 1 ml, 2 ml, etc., are collected. Use these data to construct a graph of temperature versus cumulative volume. This curve indicates the boiling point of components since, at these boiling points, the volume increases without a corresponding increase in temperature. If the graph is drawn as the distillation proceeds, the fractions can be chosen so that each component is represented by a fraction. Of course, there will also be fractions which are between the steps and are mixtures of components.

Collect sufficient fractions so that the change in constants from fraction to fraction can be evaluated.

In addition to the preceding information, it is helpful to have as much data as possible on the original solvent. The following system will give much information which cannot be obtained from distillation:

Determine specific gravity, Z value, and refractive index of the original solvent.

Add 20 ml of the original solvent and 2.0 ml of water to a 25-ml graduate, and mix thoroughly. Read the amount of solvent which is soluble, and calculate % solubility. Determine the constants (specific gravity, Z value, and refractive index) of the supernatant (insoluble portion). Calculate the constants of the soluble portion as in the following example:

$$\text{sp gr original} - (\% \text{ insol}) \times (\text{sp gr insol}) = (\% \text{ sol}) \times (\text{sp gr sol}).$$

The solvents which are completely extracted by this procedure include acetone, methanol, ethanol, and both n- and isopropyl alcohols. Any of these, except methanol, can be recovered from the water layer by saturating it with NaOH. In difficult cases, the recovered solvent can be distilled from NaOH, using semimicro methods. The distillate, in most cases, has constants very close to the constants of the pure component.

Besides the solvents which are infinitely soluble in water, some, like ethyl acetate, butyl alcohol, and methyl ethyl ketone, can be partially extracted with water. Place the portion which remained from the first water extraction in a 100-ml graduate. Dilute to 100 ml with water, and mix thoroughly. Determine the solubility, and convert it to % solubility in terms of the original composition, as follows:

$$(\% \text{ sol}) \times (\% \text{ insol}) \text{ on 1st extraction} = \% \text{ sol in terms of original.}$$

Using the constants of the supernatant, calculate the constants for the soluble portion. If desired, separate the water layer and saturate with NaCl to salt out the soluble solvent. Dry the recovered solvent over anhydrous Na_2SO_4 and determine the constants, or distill the material.

Remember that the recovered solvent is only part of that which is present. The remainder will be entirely soluble in 80% H_2SO_4 , or in an 80:20 mixture of H_2SO_4 and H_3PO_4 .

Remove the supernatant from the water extraction, and place it in another graduate. Add an equal volume of 80% H_2SO_4 , or of an 80:20 H_2SO_4 : H_3PO_4 mixture. (The latter causes less hydrolysis of esters, so that by diluting the acid layer to 3 or 4 volumes

and saturating with Na_2SO_4 , the esters can be recovered unchanged along with the other components, except unsaturated hydrocarbons.) Mix the acid and solvent thoroughly, and determine % solubility. Convert this to % solubility in terms of the original composition, as follows:

$$(\% \text{ sol}) \times (\% \text{ water insol}) = \% \text{ solubility in terms of original.}$$

Determine the constants of the supernatant (insoluble in 80% H_2SO_4 or in 80:20 H_2SO_4 : H_3PO_4), and calculate the constants on the soluble portion.

If the solvent contains turpentine, the acid layer will be red. Esters produce an orange color, while alcohols and ketones usually give only a very light yellow. The presence of esters is also indicated by a higher calculated specific gravity than that of alcohols and ketones.

Recover the portion insoluble in 80% H_2SO_4 , place it in a graduate, and add twice the volume of fuming H_2SO_4 (30-33% free SO_3). Mix carefully and thoroughly. Determine the % solubility, and calculate it in terms of % solubility of the original. Determine the constants on the portion which is insoluble in fuming H_2SO_4 . (This must be pipetted by vacuum because of the fuming H_2SO_4 .)

The soluble portion is an aromatic or halogenated aromatic hydrocarbon, and the remainder consists of aliphatic hydrocarbons or halogenated aliphatic hydrocarbons.

Use part of the original solvent or parts of the fractions from distillation to test for esters, ketones, alcohols, and halogenated hydrocarbons. (If steam distilled, the water layer will have to be checked for methanol.)

I. TEST FOR MISCIBILITY

Apparatus

Graduated cylinders, 25 ml, glass stoppered

Pipets, 10 ml, volumetric

Reagents

Hydrochloric acid, conc. (36% HCl)

Sulfuric acid, (80% v/v)

Dimethyl sulfate (CAUTION: Keep off the skin.)

Analytical Procedure

1. Pipet a 10-ml sample into a dry, tared, graduated cylinder. Weigh and calculate the specific gravity.
2. Add 10 ml of water, and mix gently.
  - a. Complete miscibility excludes:
    - (1) Saturated aliphatic hydrocarbons
    - (2) Aromatic hydrocarbons
    - (3) Halogenated saturated aliphatic or aromatic hydrocarbons
    - (4) Organic acids
    - (5) Weakly acidic compounds, such as:
      - (a) Phenols
      - (b) Enols
      - (c) Primary and secondary nitro compounds
      - (d) Oximes
      - (e) Amino acids
    - (6) Neutral compounds
3. Add 10 ml of solvent to 10 ml of conc. HCl (or 80% H₂SO₄); mix gently by inverting several times. Let settle, and note the volumes.
  - a. Complete miscibility includes:
    - (1) Alcohols
    - (2) Esters
    - (3) Aldehydes
    - (4) Ketones
    - (5) Unsaturated compounds
    - (6) Anhydrides
    - (7) Ethers
    - (8) Quinones
  - b. Complete insolubility includes:
    - (1) Saturated aliphatic and aromatic hydrocarbons
    - (2) Halogenated saturated aliphatic and aromatic hydrocarbons

4. Cautiously add a 10-ml sample to 10 ml of dimethyl sulfate in a graduated cylinder. Stopper and invert several times to mix. (Watch for pressure when relieving the stopper.)

NOTE: Solubility is an index to the aromatic content. If, however, the solubility exceeds 25%, dilute the sample accurately with heptane, benzene, or petroleum ether; and repeat the procedure.

Calculations For Miscibility

$$\% \text{ miscibility} = \frac{(\text{vol orig} - \text{vol final})}{\text{vol orig}} \times 100$$

II. BEILSTEIN TEST FOR HALOGENATED HYDROCARBONS

Analytical Procedure

1. Prepare a small copper wire, supported in a glass tubing handle, with a small loop at the end.
2. Heat the wire until only a yellow flame exists. To avoid melting the wire, use the edge of the flame.
3. Cool the wire loop. Dip it into the sample.
4. Heat the sample in the edge of the flame. A green color indicates a halogen.

III. DETERMINATION OF AROMATIC CONTENT BY REFRACTIVE INDEX AND DISPERSION MEASUREMENT

Apparatus

Refractometer. Abbe type

Graph paper, rectangular

Reagents

Benzene, pure

Isooctane (2,2,4-trimethylpentane), pure

Standards, 20%, 40%, 60%, and 80% mixtures (by volume) of benzene in isooctane

Analytical Procedure

1. Using the refractometer, determine the index of refraction and dispersion values for the standards and the unknown sample.
2. Plot index versus % aromatic for the standards.
3. Determine the specific dispersion, using the refractometer nomograph and the density of the samples.
4. Plot specific dispersion.
5. Compute the aromatic composition of the unknown, using the two graphs.

IV. DETERMINATION OF METHYL KETONES

Apparatus

Spot plate, white

Reagents

Sample solvent

Acetone

Sodium nitroprusside (5%)

Sodium hydroxide (30%)

Acetic acid, glacial

Analytical Procedure

1. Into separate spot-plate depressions, place 1 drop of aqueous or alcoholic sample and 1 drop of acetone, for comparison. Add 1 drop of 5% sodium nitroprusside and 1 drop of 30% NaOH.
2. After a short time, add 1 or 2 drops of acetic acid.
3. A purple color indicates the presence of a methyl ketone.

V. DETERMINATION OF ESTERS

Apparatus

Crucible, porcelain, 20-ml volume

Micro burner + porcelain triangle

Ring stand for triangle support

Reagents

Hydroxylamine, saturated alcoholic solution

Potassium hydroxide, saturated alcoholic solution

Hydrochloric acid (0.5N) - Dilute 4.1 ml of conc. HCl to 100 ml.

Ferric chloride solution (1%) - Dissolve 1 g of FeCl_3 in 100 ml of water.

Amyl acetate

Analytical Procedure

1. To 1 drop of dry unknown in a crucible, add 1 drop of $\text{NH}_2\text{OH} \cdot \text{HCl}$ and 1 drop of KOH. Heat until bubbling begins.
2. Cool, and add 1 drop of HCl and 1 drop of FeCl_3 .
3. An intense violet color indicates the presence of an ester.
4. To 1 drop of amyl acetate, add 1 drop of $\text{NH}_2\text{OH} \cdot \text{HCl}$ and 1 drop of KOH. Heat, and then cool and add 1 drop of HCl and 1 drop of FeCl_3 . Note the color for comparison with the sample.

VI. DETERMINATION OF ALCOHOLS (CERATE TEST)

Reagents

Ceric nitrate reagent - Dissolve 90 g of ceric ammonium nitrate in 225 ml of warm 2N HNO_3 .

Analytical Procedure

1. Add 0.5 ml of ceric nitrate reagent to 2 ml of an aqueous solution of the unknown in a test tube. Shake.
2. In the presence of alcohols, glycols, hydroxy acids, hydroxy esters, and hydroxy aldehydes and ketones that contain no more than 10 carbon atoms, the solution changes from a bright yellow to amber, yellow-orange, or red. (Note that phenols produce a green-brown or brown precipitate.)

VII. DETERMINATION OF METHANOL

Apparatus

Spectrophotometer, Hewlett-Packard Model 8450A

Graduated cylinders, glass-stoppered, 25 or 100 ml

Pipets

Reagents

Ethanol

Potassium permanganate reagent - Dissolve 3 g of KMnO_4 in 15 ml of 85% H_3PO_4 , and combine with 85 ml of distilled water.

Oxalic acid reagent - Dissolve 5 g of oxalic acid in 100 ml of 1:1 H_2SO_4 .

Schiff's reagent, modified - Add 0.2 g of fuchsin to 120 ml of hot water, cool, and add a solution of 2 g of anhydrous sodium bisulfite in 20 ml of water. Mix thoroughly. Add 2 ml of conc. HCl , and dilute to 200 ml with water. Store in a well-stoppered brown bottle in the refrigerator. If any residual color remains in the reagent, remove it by passing a stream of SO_2 through the reagent.

Standard methanol solution (5 mg methanol/ml) - Dilute 1 ml of methanol to 200 ml with distilled water.

Analytical Procedure

1. Add 0.25 ml of ethanol to 5 ml of aqueous unknown in a 25-ml graduated cylinder; mix and add 2 ml of KMnO_4 reagent.

2. Allow to set for 10 minutes.
3. Decolorize the solution with 2 ml of oxalic acid reagent.
4. Add 5 ml of Schiff's reagent, mix, and allow to set for one hour. Read the absorbance at 570 nm.
5. Compare with standard methanol (1-2.5 mg), treated the same way and at the same time.
6. A violet color indicates methanol.
7. If the color is too intense, dilute the entire sample to 100 ml with water; and read again.

VIII. MISCELLANEOUS TECHNIQUES

Instrumental analytical techniques have become extremely helpful in product identification. The following table indicates a possible approach:

TYPE	METHODS TO BE TRIED
Organic liquid	Gas chromatography, infrared analysis of GC fractions, fractional distillation, density, refractive index, infrared analysis of fractions
Organic solid	KBr pellet infrared, Soxhlet extraction, organic qualitative scheme, inorganic cations & anions
Inorganic liquid (Water solution) & inorganic solid	Anion qualitative scheme, atomic absorption, ICP
Glues, emulsions, soaps, etc.	Solvent extraction, gas chromatography, infrared analysis, ASTM standard methods

After the analysis of a product, it is sometimes of great value to synthesize it on the basis of the determined constituents. For example, if a commercial paint solvent is found to consist of five components, each contributing 20% to the total mixture, a synthetic sample can be made for comparison of the infrared spectrum. Any previously undetected component or any variation in quantitative ratios will be evident immediately.

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FLASH-POINT TESTING WITH PENSKY-MARTENS CLOSED FLASH TESTER

ABSTRACT

This method describes the Pensky-Martens closed flash tester, as used in ASTM Method D93-62, "Test for Flash Point by Pensky-Martens Closed Tester."

APPLICATIONS AND LIMITATIONS

Flash-point determination measures the tendency of a sample to form a flammable mixture with air. It can also indicate the possible presence of volatile contaminants in a relatively nonvolatile material. The procedure is used on fuel oils, as well as viscous materials and suspensions of solids, but is not applicable to drying oils, solvent-type liquid waxes, or cut-back asphalts. (Use ASTM D-1310.)

ES&H NOTES

Keep the flash point tester well shielded and apply the flame cautiously to avoid causing an external fire.

APPARATUS

Pensky-Martens tester, ASTM Specification E-134

Thermometers, range 20-230°F and 200-700°F

ANALYTICAL PROCEDURE

1. Fill the cup with the material to be tested to the level indicated by the filling mark. Place the lid on the cup, set the cup on the stove, and lock it into position.
2. Insert the thermometers, and light the test flame.
3. Turn on the stirrer, and apply heat at such a rate that the temperature, as read on the thermometer, increases 9-11°F per minute.
4. Apply the test flame by operating the mechanism on the cover which controls the shutter; and test the flame burner so that the flame is lowered into the vapor space of the cup in 0.5 seconds, left in its lowered position for 1 second, and quickly raised to its high position.

5. The flash point is the temperature read on the thermometer at the time the test flame application causes a distinct flash in the interior of the cup. Sometimes the test flame during application is surrounded with a bluish halo as the flash-point temperature is approached. Do not confuse the true flash with this halo.

CALCULATIONS

Observe and record the barometric pressure. For each 25 mm below the 760-mm barometric reading, add 1.5°F to the flash point. For each 25 mm above 760 mm, subtract 1.5°F from the flash point.

REFERENCES

1. "Standard Test Methods for Flash Point by Pensky-Martens Closed Tester," ASTM Standard D 93-85 in Vol. 6.03 Paints, Related Coatings, and Aromatics (Philadelphia: American Society for Testing and Materials, 1987).

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FORMALDEHYDE IN AIR

ABSTRACT

Formaldehyde reacts with a chromotropic acid-sulfuric acid solution to form a stable, purple-colored complex, which can be measured colorimetrically at 580 nm.

APPLICATIONS AND LIMITATIONS

The analytical range for an 80-liter air sample is 0.02 to 0.4 PPM. For greater accuracy, the formaldehyde standard solution should be standardized (see Reference 1).

Phenols interfere, but little interference is seen from other aldehydes. Alcohols, olefins, and aromatic hydrocarbons produce very small interferences.

ES&H NOTES

Formaldehyde is designated as a Class A2 carcinogen by the ACGIH and a Class 2A carcinogen by the IARC. This material should be handled in a Designated Area, typically a laboratory hood. The room and/or hood shall be clearly labeled with a sign indicating that a carcinogen is in use.

APPARATUS

Spectrophotometer, Hewlett-Packard Model 8450A

Midget bubblers, all glass

Assorted laboratory glassware

REAGENTS

Sodium bisulfite (1%) - Dissolve 1 g of NaHSO_3 in 100 ml of distilled water. PREPARE FRESH WEEKLY.

Chromotropic acid (1%) - Dilute 0.10 g of 4,5-dihydroxy-2,7-naphthalene disulfonic acid disodium salt to 10 ml with water. Filter and store in a brown bottle. PREPARE FRESH WEEKLY.

Sulfuric acid, conc. (96% H_2SO_4)

Aldehyde-free water - Boiled, doubly-distilled water

Formalin solution, 37% formaldehyde (37 g HCHO/100 ml of solution)

Formaldehyde stock solution (1 mg HCHO/ml) - Dilute 2.7 ml of formalin solution to 1000 ml with distilled water.

Formaldehyde standard solution (10 µg/ml) - Dilute 1 ml of formaldehyde stock solution to 100 ml with 1% sodium bisulfite. PREPARE FRESH WEEKLY.

ANALYTICAL PROCEDURE

1. Collect the sample in a midget bubbler, using 15 ml of a 1% sodium bisulfite solution as a collecting medium. Collect at least 100 L of air. Note the volume of each impinger.
2. Pipet 4-ml aliquots from each sample solution into 40-ml centrifuge tubes.
3. Add 0.1 ml of 1% chromotropic acid to the tubes and mix.
4. Slowly add 6 ml of conc. H_2SO_4 to the tubes. Let the color develop for 30 minutes, while the tubes cool to room temperature. Transfer the solution to absorbance cells, and read the absorbance at 580 nm. If the absorbance is too high, dilute a smaller aliquot to 4 ml with 1% sodium bisulfite and analyze.
5. Prepare a series of standards containing from 1 to 20 µg of formaldehyde (0.1 to 2.0 ml of standard solution) in enough 1% sodium bisulfite to yield 4 ml of solution. Proceed as in Step 2.
6. Plot absorbance versus concentration in µg of formaldehyde/4 ml.
7. Determine the amount of formaldehyde present in the samples from the standard curve.

CALCULATIONS

$$\text{mg formaldehyde/m}^3 = \frac{\mu\text{g formaldehyde from calibration curve}}{\text{Vol of air sampled in liters at STP}}$$

REFERENCES

1. "Formaldehyde," NIOSH Manual of Analytical Methods, Vol. 1, U.S. Department of Health and Human Services Publication No. 84-100, ed P.M. Eller (3rd ed; Washington, DC: U.S. Government Printing Office, 1984), Method 3500.
2. "Tentative Method of Analysis for Formaldehyde Content of the Atmosphere (Colorimetric Method)," Methods of Air Sampling and Analysis, ed M. Katz (2nd ed; Washington, DC: American Public Health Association, 1977), Method 116.

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OIL MIST IN AIR

ABSTRACT

Air samples are collected on Whatman No. 41 filter paper, 37-mm membrane filters, or electrostatic precipitators (ESP); or by suitable organic solvents. The oil mist is extracted or washed into an organic solvent and quantitated using either Fourier transform infrared or ultraviolet spectrophotometry.

APPLICATIONS AND LIMITATIONS

The working range for this technique, using infrared spectrophotometry, is 0.1 to 2.5 mg per sample, assuming a sampling flow rate of 1-2 liters/minute.

APPARATUS

Fourier transform infrared spectrometer, Bio-Rad Model FTS-7 with NaCl cells

Ultraviolet spectrophotometer, Hewlett-Packard Model 8450A, with silica cells

Cellulose membrane filters, 37 mm (0.8 micron)

ESP collection kit

Whatman No. 41 filter paper, 47 mm

Assorted laboratory glassware

REAGENTS

Solvents, such as ether, carbon tetrachloride, isooctane, chloroform, trichlorotrifluoroethane, etc.

Oil standard (100 mg/ml) - Weigh 10 g of the oil being sampled into 100 ml of a suitable solvent.

ANALYTICAL PROCEDURE

1. Prepare 1- to 100- μ g/ml standards of the oil in question in a suitable solvent.
2. Transfer the collected samples into scintillation vials, and extract the oil using 20 ml of the same solvent used to prepare the standards.

3. Record the spectra at the particular wavelength at which the oil has maximum absorbance.
4. Measure the Desorption Efficiency (DE) for each oil at least once for each lot of filters. Deposit a known amount of oil onto a filter; evaporate the solvent and allow to stand overnight; desorb and analyze as in Steps 1-3. The desorption efficiency is the ratio between the amount of analyte recovered and the amount deposited (see Reference 1).
5. Quantitatively determine the amount of oil, using the standards for that oil, by plotting the peak height versus concentration in µg/ml.

CALCULATIONS

$$\text{mg oil/m}^3 = \frac{\mu\text{g oil from curve}}{\text{liters of air sampled}} \div \text{DE} \times \text{dilution factor (if any)}$$

REFERENCES

1. "Mineral Oil Mist," NIOSH Manual of Analytical Methods, Vol. 1, U.S. Department of Health and Human Services Publication No. 84-100, ed P.M. Eller (3rd ed, Suppl 2; Washington, DC: U.S. Government Printing Office, 1987), Method 5026.
2. E.M. Ray, "Sampling and Determination by Ultraviolet Absorption of Oil Mists and Solvent Vapors," Am Ind Hyg Assoc J 31:472 (1970).
3. M. Lippman and D.H Goldstein, "Oil-Mist Studies, Environmental Evaluation and Control," Arch Environ Health 21:591 (1970).

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ORGANIC SOLVENTS IN AIR

ABSTRACT

A known volume of air is drawn through a sorption tube or a 3M Company Organic Vapor Badge to trap the organic vapors present. The sorbant is transferred to a graduated cylinder and desorbed with carbon disulfide. An aliquot is injected into a gas chromatograph, and the area of the resulting peak is determined and compared with areas obtained from the injection of standards.

APPLICATIONS AND LIMITATIONS

The sampling device is small and portable and involves no liquids. The 3M Vapor Badges are easier to use, since there is no need to calibrate a sampling pump. However, since they are passive devices, sampling times are generally longer than those required for the sorption tubes.

Interferences are minimal, and most of those which do occur can be eliminated by altering the chromatographic conditions. Precision of the analytical method is $\pm 7\%$.

A disadvantage of the method is that the amount of sample which can be absorbed is limited by the number of milligrams that the sorbant in the tube or badge will hold before overloading. When the amount of water in the air is so great that condensation occurs, organic vapors will not be trapped. When two or more solvents are known or suspected to be present in the air, such information, including their suspected identities, should be transmitted with the sample since, with differences in polarity, one may displace another from the sorbant.

It must be emphasized that any compound having the same retention time as the specific compound under study at the operating conditions described in this method is an interference. Hence, retention-time data on a single column, or even on a number of columns, cannot be considered as proof of chemical identity. For this reason, it is important that a sample of the bulk solvent(s) be submitted at the same time so that identities can be established by other means.

ES&H NOTES

A number of organic solvents are designated as carcinogens, suspect carcinogens, or reproductive hazards. These materials should be handled in a Designated Area, typically a laboratory hood. The room and/or hood shall be clearly labeled with a sign indicating that a carcinogen or particularly hazardous material is in use.

In addition, many organic solvents are highly flammable. Carbon disulfide, the preferred desorbant for this procedure is both highly flammable and acutely hazardous.

APPARATUS

3M Organic Vapor Badges #3500 - Model 3500 badges are nonspecific, absorbing several organic vapors simultaneously (see Reference 1).

Charcoal tubes - Glass tube with both ends flame sealed, containing two sections of a sorbent material (i.e., activated charcoal, silica gel, Chromosorb, etc.) separated by a 2-mm portion of urethane foam. A 3-mm portion of urethane foam is placed between the outlet end of the tube and the backup section. A plug of glass wool is placed in front of the absorbing section. Most of the tubes used are non-specific, absorbing several organic vapors simultaneously.

Gas chromatograph, Hewlett-Packard Model 5880A, equipped with a flame ionization detector

Column (20 ft x 1/8 in) with GP 10% SP-1000 stationary phase on 80/100 mesh Supelcoport solid support (Supelco, Inc.)

Disposable glassware, such as 20 ml glass vials, for standards and sample preparation

Hamilton syringes, 10 μ l

Pipets or repipetors of appropriate volumes

Recorder and some method for determining peak area

REAGENTS

Carbon disulfide, Spectrograde

Methylene chloride

Nitrogen, purified

Hydrogen, prepurified

Compressed air, filtered

Bulk sample of the compound under study

ANALYTICAL PROCEDURE

1. Preparation of the samples:

Sorbent tubes: Remove and discard the glass wool in front of the first section of sorbent. Transfer the sorbent in the first (larger) section to a disposable glass container with a lid. Remove and discard the separating section of foam, and transfer the second section to another container. Alternatively, combine both sections in the same container.

Add a known volume (usually 5 ml) of CS₂ or methylene chloride to each container. Maximum desorption occurs in about 30 minutes when the sample is occasionally gently agitated; if the sample is not agitated, complete desorption requires 3 hours.

3M Vapor Badges: Open the badge, and transfer the sorbent material to a glass container. Add a known volume (usually 5 ml) of an appropriate solvent, usually CS₂ or methylene chloride (see Reference 1). Maximum desorption occurs in about 30 minutes when the sample is occasionally gently agitated. Alternatively, inject the solvent directly into the badge, and allow to desorb for 30 minutes. Withdraw an aliquot from the badge for injection.

2. GC conditions: The typical operating conditions for the gas chromatograph are:

- a. Nitrogen gas flow: 85 cc/min (70 psig)
- b. Hydrogen gas flow to detector: 65 cc/min (24 psig)
- c. Air flow to detector: 500 cc/min (50 psig)
- d. Injector temperature: 200°C
- e. Manifold detector temperature: 250°C
- f. Isothermal oven or column temperature: Refer to Table C-1 for specific compounds. For compounds not found in the Table, see Reference 2 or 3.

3. Injection: The first step in the analysis is the injection of the sample into the GC. To eliminate difficulties arising from blowback or distillation within the syringe needle, use the solvent flush injection technique. First flush the 10- μ l syringe with solvent several times to wet the barrel and plunger. Immerse the needle in the sample and withdraw a known (usually 4- μ l) aliquot. After removing the needle from the sample prior to injection, pull back the plunger a short distance to minimize evaporation of the

sample from the tip of the needle. Run duplicate injections of each sample and standard. No more than a 3% difference in area is to be expected.

4. Area measurement: Measure the area of the sample peak using an electronic integrator or some other suitable form of area measurement. Read the preliminary results from a standard curve prepared as discussed below.
5. Measurement of Desorption Efficiency (DE): Measure the desorption efficiency for each compound at least once for each lot of tubes or monitors. Inject a known amount of analyte into a tube or monitor, allow to stand overnight, desorb, and analyze. The desorption efficiency is the ratio between the amount of analyte recovered and the amount injected. (See Reference 2 for details.)
6. Standard calibration: It is convenient to express the concentration of the standards in terms of mg per known volume of desorbant used. Use the density of the specific compound to convert mg to microliters for easy measurement with a microliter syringe. The use of a single standard is sufficient if the standard curve is known to be linear in the range of interest. If the curve is nonlinear, or linearity has not been determined, prepare and analyze a series of standards, varying in concentration over the range of interest, under the same GC conditions and during the same time period as the unknown samples. Plot concentration in mg CS₂ versus peak area.

NOTE: Since no internal standard is used in this method, analyze standard solutions at the same time that the sample analysis is done. This will minimize the effect of day-to-day variations of the FID response.

CALCULATIONS

1. If not using a standard curve, calculate a Response Factor for each compound analyzed, as follows:

$$\text{Response factor (RF)} = \frac{\mu\text{l standard added} \times \text{density}}{\text{peak area for standard}}$$

Then, mg of sample, mg_s = RF x peak area for sample.

2. If using a standard curve, read the weight in mg corresponding to each peak area from the curve for the compound of interest. No volume corrections are needed, because the volumes of samples and standards injected are identical.

3. For either procedure, correct each sample for the desorption efficiency and the blank, as follows:

$$\text{DE-corrected mg(DE)} = \text{mg}_s / \text{DE}$$

$$\text{Blank-corrected mg} = \text{mg(DE)} - \text{mg}_b$$

where

$$\text{mg}_s = \text{mg found in the sample tube}$$

$$\text{mg}_b = \text{mg found in the blank tube.}$$

If running the two sorbent sections separately, add the corrected amounts present in the front and backup sections of the same sample tube to determine the total measured amount in the sample.

4. For sorbent tubes, calculate the concentration in air, as follows:

$$\text{mg/m}^3 = \mu\text{g/L} = \frac{\text{total mg} \times 1000}{\text{vol of air in liters at STP}}$$

5. Calculation of contaminant concentrations for 3M Organic Vapor Badges requires the incorporation of a "calculation constant," which can be found in Reference 1.

REFERENCES

1. 3M Organic Vapor Monitor #3500 Compound Guide Notebook (St. Paul, MN: 3M Occupational Health and Safety Products Division, 1982).
2. "Organic Solvents in Air," NIOSH Manual of Analytical Methods, Part I, U.S. Department of Health, Education, and Welfare Publication No. 77-157-A, ed D.G.Taylor (2nd ed; Washington, DC: U.S. Government Printing Office, 1977), Method 127.
3. "Hydrocarbons, Halogenated," NIOSH Manual of Analytical Methods, Vol. 1, U.S. Department of Health and Human Services Publication No. 84-100, ed P.M. Eller (3rd ed, Suppl 2; Washington, DC: U.S. Government Printing Office, 1987), Method 1003.
4. "Hydrocarbons, Aromatic," NIOSH Manual of Analytical Methods, Vol. 1, U.S. Department of Health and Human Services Publication No. 84-100, ed P.M. Eller (3rd ed; Washington, DC: U.S. Government Printing Office, 1984), Method 1501.

5. "Dioxane," NIOSH Manual of Analytical Methods, Vol. 1, U.S. Department of Health and Human Services Publication No. 84-100, ed P.M. Eller (3rd ed, Suppl 1; Washington, DC: U.S. Government Printing Office, 1985), Method 1602.
6. L.D. White et al., "A Convenient Optimized Method for the Analysis of Selected Solvent Vapors in the Industrial Atmosphere," Amer Ind Hyg Assoc J 31:225 (1970).

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TABLE C-1
ORGANIC SOLVENT PARAMETERS (a)

ORGANIC SOLVENT	RANGE OR LIMITS (mg/SAMPLE)		MIN. SAMPLE VOL. (b)	GC COLUMN TEMPERATURE (°C)	MOLECULAR WEIGHT
	LOWER	UPPER			
Benzene	0.01	10	0.5	90	78.1
Carbon tetrachloride	0.20	10 (est)	10	60	154.0
Chloroform	0.10	10 (est)	0.5	80	119
p-Dioxane	0.05	10 (est)	1	100	88.1
Ethylene dichloride	0.05	10 (est)	1	90	99.0
Methyl ethyl ketone	0.01	9	0.5	80	72.1
Styrene	0.10	15	1.5	150	104
Tetrachloroethylene	0.06	21	1	130	166
1,1,1-trichloroethane (Methyl Chloroform)	0.05	11	0.5	150	133
1,1,2-trichloroethane	0.05	10	10	150	133
Trichloroethylene	0.05	13	1	90	131
Toluene	0.01	12	0.5	120	92.1
Xylene	0.02	10	0.5	100	106

- (a) See Reference 2.
 (b) Minimum volume, in liters, required to measure 0.1 times the OSHA limit.
 Maximum volume in all cases is 10L. All volumes quoted assume 760 mm Hg and 25°C.

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PCB'S IN OIL

ABSTRACT

The presence of polychlorinated biphenyls (PCB's) in waste oil streams must be determined in order to select the proper method of cleanup or disposal. The analytical technique used in the Industrial Hygiene Chemistry Lab emphasizes screening of samples, using Fourier transform infrared spectroscopy (FTIR) for gross screening and gas chromatography (GC) for verification and semiquantitation.

APPLICATIONS AND LIMITATIONS

The FTIR is used to screen samples for PCB's in the thousand PPM range. If no PCB's are indicated by this technique, the samples are extracted in hexane and run on the GC. Depending upon the sample quality and size, the detection limit for the GC is 5-10 PPM.

The technique is limited by several factors: (1) The chromatographic column can be overloaded fairly easily, causing several hours to days delay while it is cleaned up. This problem is the reason for pre-screening the samples using the IR. (2) Samples may contain degraded PCB's (having non-standard peak patterns) or solvents and/or water as contaminants (making them difficult to clean up); both problems can obscure the identification of the PCB peaks. (3) Sample runs on the IR take about 15 minutes; those on the GC, about 45 minutes, limiting the number of samples that can be run in a day. (4) Finally, this technique, as practiced in our laboratory, does not meet EPA requirements for the quantitation of PCB's.

ES&H NOTES

Polychlorinated biphenyls are designated as Class 2A carcinogens by the IARC. These materials should be handled in a Designated Area, typically a laboratory hood. The room and/or hood shall be clearly labeled with a sign indicating that a carcinogen is in use.

APPARATUS

Gas Chromatograph, Hewlett-Packard Model 5880A with Electron Capture Detector and Integrator

Fourier transform infrared spectrophotometer, Bio-Rad Model FTS-7

Balance, Mettler Model AE163, weighing to 0.1 mg

Pipettes, disposable

Salt plates for the FTIR, sodium chloride or potassium bromide

Scintillation vials

Syringes, 10 μ l, liquid

REAGENTS

Hexane, Pesticide grade

Arochlor standards, most commonly those designated 1242, 1254, and 1260

ANALYTICAL PROCEDURE

Infrared Spectroscopy

1. Place a drop of oil on a salt plate. If the sample consists of more than one layer, sample only the top layer.
2. Assemble the sample cell, place it in the sample compartment, and scan the FTIR spectrum. The run will take less than 1 minute.
3. The major characteristic peaks for PCB's occur at 755, 780, 810, 880, 1028, 1095, 1135, and 1750 cm^{-1} .
4. If no PCB's are detected, the oil samples must be extracted with hexane and run on the gas chromatograph.

Sample preparation

1. Weigh and tare a scintillation vial.
2. Pipette approximately 0.1 g of oil into the vial, and record the weight.
3. Add exactly 10 ml of hexane and extract for 2-3 hours, agitating occasionally. The sample is now ready for gas chromatographic analysis.

Gas Chromatography

1. GC conditions: Operating conditions for the GC are as follows:
  - a. Column: 6 ft x 4 mm packed glass containing Supelco 1.5% SP-2250 / 1.95% SP-2401 on 100/120 mesh Supelcoport
  - b. Detector: Electron capture
  - c. Nitrogen gas flow: The flow should be such that the hexane peak elutes at an approximate relative retention time of 0.5 sec at 42 psig (~ 90-100 cc/min).
  - d. Oven temperature: 200°C
  - e. Detector temperature: 300°C
  - f. Injector temperature: 250°C
2. Analysis
  - a. Turn on the Nitrogen gas flow, then the gas chromatograph. From the PCB Program Tape, get ANALYSIS "REVMXPCB2/83". This program contains the operating conditions for the instrument and the calibration factors for the PCB peaks. Allow the instrument to warm up until a stable baseline is achieved (15-20 minutes).
  - b. Get PRGM "GRAYREVMXPCB2/83", which starts the analysis and prints out the analytical results. Remove the Program Tape, and insert the PCB Data Tape. All chromatographic information is stored on the tape and is available for later manipulation.
  - c. Rinse a 10- μ l glass syringe 5-10 times with the sample to be analyzed. Draw up 1.8 μ l of sample, then draw back the plunger until air enters the barrel. This will minimize evaporation of the sample from the needle during injection.
  - d. Be sure the autosampler is in position 1. After answering the appropriate questions for the data system, carefully inject the sample into Injector A. The sample run will take about 45 minutes.
  - e. The analytical program prints out a chromatogram and, for each peak, the retention time, peak area, and percent of total area.

3. Quantitation

- a. After determining from the initial chromatogram that PCB's are probably present, another sample must be run for quantitative analysis. The sample may be either diluted further or made up as a more concentrated hexane solution (a larger amount of oil in the 10 ml of hexane). It may be necessary to clean up the sample using a Fluorosil column before quantitation (see Reference 3).
- b. Proceed as in the Analysis Section, injecting 2.8 μ l of sample into the GC. All calculations are based upon a 2.8- μ l injection and 10 ml of hexane.
- c. The quantitative report identifies the predicted PCB and peak number and the nanograms represented by each peak. The program then calculates total PPM of PCB's by weight.
- d. In addition, to assure that the computer program has correctly interpreted the data, compare the chromatogram with those of individual Arochlor standards. The peak patterns must match in order to successfully identify a given PCB.
- e. Occasionally run known Arochlor standards to check the calculations.

REFERENCES

1. "Polychlorobiphenyls," NIOSH Manual of Analytical Methods, Vol. 1, U.S. Department of Health and Human Services Publication No. 84-100, ed P.M. Eller (3rd ed, Suppl 2; Washington, DC: U.S. Government Printing Office, 1987), Method 5503.
2. "Standard Method for Analysis of Polychlorinated Biphenyls in Insulating Liquids by Gas Chromatography," ASTM Standard D 4059-86 in Vol. 10.03 Electrical Insulating Liquids and Gases (Philadelphia: American Society for Testing and Materials, 1987).
3. "Organochlorine Pesticides and PCB's," Test Methods for Evaluating Solid Waste, Physical/Chemical Methods, U.S. Environmental Protection Agency Publication No. SW-846 (3rd ed; Washington, DC: U.S. Government Printing Office, 1986), Method 8080.
4. R.G. Webb and A.C. McCall, "Quantitative PCB Standards for Electron Capture Gas Chromatography," J Chromatog Sci 11(7):366 (1973).

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TRICHLOROACETIC ACID IN URINE

ABSTRACT

Certain chlorinated hydrocarbons, aldehydes, and acids undergo the Fujiwara pyridine-alkali reaction, which produces a characteristic pink color. Estimation of exposures to trichloroethylene by urine analysis is carried out by development of a pyridine-potassium hydroxide plus trichloroacetic acid (TCA) complex in an aliquot of raw urine. The complex concentration is measured at 530 nm. The environmental health action level for trichloroacetic acid in urine is 15 mg/liter.

APPLICATIONS AND LIMITATIONS

The absorbance produced by trichloroacetic acid following the Fujiwara reaction appears to be linear between 0 and 0.6 mmoles. However, the procedure is not specific for TCA. Chloroform, chloral hydrate, and unreacted trichloroethylene produce similar absorbances. Trichloroethanol does not interfere.

APPARATUS

Spectrophotometer, Hewlett-Packard Model 8450A

Assorted laboratory glassware

REAGENTS

Toluene

Potassium hydroxide (3.3M) - Dissolve 185 g of KOH in 1 liter of distilled water.

Pyridine

Trichloroacetic acid stock solution (1000 µg TCA/ml) - Dissolve 1.0 g of TCA in 1 liter of distilled water. Standardize by titration with standard alkali.

Trichloroacetic acid standard (50 µg TCA/ml) - Dilute 5 ml of TCA stock solution to 100 ml with distilled water.

ANALYTICAL PROCEDURE

1. Mix 1 ml of toluene, 5 ml of 3.3M KOH, and 5 ml of pyridine in a 40-ml centrifuge tube.
2. Add 1 ml of urine, and place the tube in a boiling-water bath for 3 minutes.
3. Cool immediately in an ice-water bath.
4. Treat a blank and standards of 10, 25, and 50 μ g TCA in the same manner, i.e., add 1 ml of standard + 5 ml of 3.3M KOH + 5 ml of pyridine.
5. Remove the tubes from the ice bath when cool, and pipet 2 ml of the organic phase into a 40-ml centrifuge tube containing 2 ml of distilled water. Mix well.
6. Measure the absorbance of the blank, standards, and samples at 530 nm within 10 minutes of final mixing.

CALCULATIONS

Plot μ g TCA versus absorbance of the standards. Read the sample concentration from this standard curve.

$$\text{mg TCA/liter urine} = \mu\text{g TCA in 1-ml urine aliquot}$$

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1. T.A. Seto and M.O. Schultze, "Determination of Trichloroethylene, Trichloroacetic Acid, and Trichloroethanol in Urine," Anal Chem 28:1625 (1956).
2. H.B. Elkins, The Chemistry of Industrial Toxicology (New York: J. Wiley & Sons, Inc., 1959), p. 405.

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SECTION D

GENERAL RADIOCHEMICAL PROCEDURES

A number of chemical procedures are used by the Sandia Laboratories Industrial Hygiene Chemistry Laboratory for the analysis of radioactive materials. Sandia Laboratories has maintained an environmental monitoring program (soil, water, and vegetation) since 1959. This program determines whether there is increased radiation exposure to the general public and to what magnitude. A number of routine measurements are made for gross alpha and beta activity in environmental samples.

Personnel working with radioactive materials, such as uranium and tritium, are occasionally sampled for the analysis of body fluids or wastes to detect possible exposure to radioactive materials. The information obtained is valuable when exposure has been due to radioisotopes that do not emit penetrating gamma radiation.

Other routine radiochemical survey programs consist of analyses of swipes for tritium and of gross alpha and beta counting of swipes and air filters for surface contamination.

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ENVIRONMENTAL SAMPLES

VEGETATION SAMPLES

A separate aliquot of the vegetation samples is taken for each radiochemical analysis. Air dry a 100-g aliquot of vegetation (if available) to a constant dry mass. Finely grind the dry sample, and place it in a 500-ml Marinelli beaker for gamma spectrum analysis. Heat a second 100-g aliquot with cyclohexane in a 1000-ml distillation flask, and collect the water in a Barrett trap. Analyze a 1-ml sample of the collected water for tritium using a liquid scintillation counter (see "Tritium in Urine and Water and on Swipes," Section D of this Manual).

SOIL SAMPLES

To analyze soil samples for tritium, heat 100-g aliquot with cyclohexane in a 1000-ml distillation flask, and collect the water in a Barrett trap. Analyze a 1-ml sample of the collected water for tritium using a liquid scintillation counter (see "Tritium in Urine and Water and on Swipes," Section D of this Manual). Uranium analysis of soils by laser phosphorimetry is described in "Total Uranium in Soil, Urine, and Water," Section D of this Manual.

WATER SAMPLES

To analyze water samples for gross alpha-beta activity, evaporate an aliquot of water (100 ml for alpha analysis; 400 ml for beta analysis) on a 5-cm diameter stainless steel planchet. Count the sample for 100 minutes using a low-background, gas-proportional detector. Calibrate and check the detector routinely using NBS-traceable radionuclide standards (see "Gross Alpha and Beta Activity in Water," Section D of this Manual).

GAMMA RADIATION

Analyze water, soil, and vegetation samples for gamma-emitting radionuclides using the American National Standards Institute/Institute of Electrical and Electronics Engineers (ANSI/IEEE) Standard 680-1978 (Standard Techniques for Determination of Germanium Semiconductor Detector Gamma Ray Efficiency Using a Standard Marinelli Beaker Geometry). Place approximately 450 g of water, 800 g of soil, or 100 g of vegetation in 500-ml Marinelli beakers and count for 1000 minutes (100 minutes for soil) using high-efficiency, high-resolution intrinsic Ge or Ge(Li) detectors and multi-channel analyzers. Calibrate and check the detectors routinely using either a mixed radionuclide

standard obtained from the National Institute of Standards and Technology (NIST) or an NIST-traceable standard for specific radionuclides. The data are analyzed by computer software developed by Canberra Industries.

REFERENCES

1. S. Hwang et al., 1989 Environmental Monitoring Report, Sandia National Laboratories, Albuquerque, New Mexico, SAND90-0301 (Albuquerque, NM: Sandia National Laboratories, 1990), Appendix C.

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GROSS ALPHA AND BETA ACTIVITY IN WATER

ABSTRACT

Gross quantities of alpha- and beta-emitting radionuclides (but not the identity of the nuclide) can be determined using a low-background internal proportional counter. A known volume of sample is concentrated and dried in a planchet before counting. Results are returned in disintegrations per minute (dpm). Tritium and other volatile radionuclides cannot be determined by this method.

APPARATUS

Planchets, stainless steel

Assorted laboratory glassware

REAGENTS

Indicator solution - Eriochrome Black T, commercially available through Van Waters and Rogers, Inc.

Buffer solution, pH 10 - Commercially available through Van Waters and Rogers, Inc.

Ethylenediaminetetraacetic acid (EDTA) disodium salt (0.01M or 0.02N) - Dissolve 3.72 g of reagent-grade Na_2EDTA in 1 liter of distilled water, and dilute to volume (1 ml is equivalent to 1 mg of CaCO_3).

Nitric acid, conc. (70% HNO_3)

Acetone

ANALYTICAL PROCEDURE

Dissolved Solids

1. Determine the hardness of the water sample by titrating a 50-ml aliquot with EDTA as follows:
  - a. To a 50-ml aliquot in a 250-ml beaker, add 4 drops of indicator and 10 drops of buffer; and swirl to mix. The solution should be wine-red.

- b. Titrate to a deep blue end-point, without the slightest trace of purple. In a 50-ml aliquot, 1 ml of titrant = 20 mg/liter or 20 PPM hardness as CaCO_3 .
2. Calculate the aliquot to be used in the gross alpha and beta determination. The final deposit on the planchet should be 4-7 mg/cm², or 80-140 mg for a 2-inch diameter planchet:

$$\text{ml aliquot for 2-inch planchet} = \frac{(110 \pm 30) \times 1000}{\text{PPM} \times 2} *$$
3. Prepare all planchets beforehand.
  - a. Wipe the outer rim with a light film of silicone stopcock grease to prevent creep of the scale during evaporation.
  - b. Weigh to the nearest 0.1 mg.
4. Thoroughly shake all samples, filter through membrane hydrosol-type filters of 0.45-micron pore size, and save the filter papers for gross alpha and beta counting of total suspended solids.
5. Transfer the calculated, filtered aliquot to an appropriately sized beaker, add 2 ml of conc. HNO_3 , and boil.
  - a. If the original aliquot is 200 ml or less, boil it down to a few ml; transfer it quantitatively onto the planchet; and evaporate it to dryness.
  - b. If the original aliquot is greater than 200 ml, boil it down to one tenth of the original volume; and transfer it to a smaller beaker. When the volume is below 20 ml, transfer by portions to the prepared 2-inch planchet. Evaporate the sample to complete dryness.
6. Reweigh the planchets and count for alpha and beta activity.

Suspended Solids

1. Transfer the membrane filter containing the suspended solids directly to a weighed planchet.

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* Since the deposit is in nitrate form and all dissolved solids will appear on the planchet, the empirical factor 2 will convert conventional hardness figures to nitrate deposit.

2. Lay the filter, solids-side down, onto the planchet, which has been wetted previously with a few drops of acetone. Fold the filter into quarters, if necessary, to make it fit. Add about 1 ml of acetone to the planchet, thoroughly wetting the filter; and let it stand until the filter is substantially dissolved.
3. Burn off the acetone, and flame the residue briefly.
4. Let cool, weigh, and count for alpha and beta activity.

REFERENCES

1. Radiochemical Analytical Procedures for Analysis of Environmental Samples, Publication No. EMSL-LV-0539-17 (Las Vegas, NV: U.S. Environmental Protection Agency, 1979).

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TRITIUM IN URINE AND WATER AND ON SWIPES

ABSTRACT

Liquid scintillation counting is a method of detecting radioactivity by means of a solution of fluors and a photomultiplier tube. The scintillation solution converts the radioactivity to light, and the phototube responds by producing a charged pulse which can be counted.

APPLICATIONS AND LIMITATIONS

The widest application of liquid scintillation counting in the Industrial Hygiene Chemistry Laboratory is the determination of tritium in biological fluids, swipes, and water. Untreated urine and water are added directly to a scintillation cocktail and counted with a scintillation spectrometer. Swipes are placed directly in counting vials and wetted with water before the scintillator fluid is added.

The lower limits of detection for liquid scintillation counting are 1 disintegration per minute (dpm) for swipes, 0.45 pCi/ml for water or urine.

ES&H NOTES

Samples with potentially-high tritium levels should be handled in such a way to avoid spreading contamination, either to the laboratory staff or on laboratory or instrument surfaces.

APPARATUS

Liquid scintillation counter, TM Analytic Mark V Model 5303

Counting vials, 7 and 20 ml, glass and polyethylene with plastic screw caps

Assorted laboratory glassware

Pipet, 1 ml liquid

REAGENTS

Opti-Fluor, commercially available from Packard Instrument Co.

Tritium standard, commercially available from Amersham (Arlington, IL), <0.07 pCi

Reference background water, commercially available from Amersham (Arlington, IL)

Quenched tritium standards, commercially available from Amersham (Arlington, IL), 7 concentrations

SAMPLE PREPARATION

Wash hands before beginning sample preparation to limit chemiluminescence from creams and oils sometimes present on hands.

Urine

1. Pipet 1 ml of urine into a polyethylene counting vial. Add 15 ml of scintillator fluid, cap, and mix thoroughly.
2. Wipe the outside of the vial to remove fingerprints.
3. Dark adapt the sample for 30 minutes before counting to eliminate interference from chemiluminescence. Alternatively, rerun the sample 3-4 times until a steady value is obtained.

Water and Other Fluids

1. Pipet 1 ml of water into a scintillation vial.
2. Add 15 ml of scintillator fluid, and mix thoroughly. Wipe the outside of the vial to remove fingerprints.

Swipes and Swabs

1. Place the swipe or swab into a glass scintillation vial.
2. Wet the swipe with 1 ml of distilled water.
3. Add 15 ml of scintillator fluid, and mix thoroughly. Wipe the outside of the vial to remove fingerprints.

Cotton Balls

1. Place the cotton ball into a glass scintillation vial.
2. Add 5 ml of distilled water, and soak for at least 1 hour, agitating occasionally.
3. Pipet 1 ml of the liquid into another vial, add 15 ml of scintillator fluid, and mix thoroughly. Wipe the outside of the vial to remove fingerprints.

ANALYTICAL PROCEDURE

1. Place the sample vials in numbered trays, starting at the end away from the number. The first 2 samples should be the standard and the sample blank. If desired, end with a Reference water blank. Place the trays in the counter.
2. Start the computer, and select the COUNTER program (#1).
3. To set up the program, select BATCHES (#1). Edit program Tritium1: NUMBER OF RUNS is generally 1 or Continuous (C), if you wish to repeat the analyses until the values stabilize. START TRAY NO. must be the first tray in the sequence.

NOTE: The usual values for the program are as follows:

ID Tritium1
Mode DPM CQ SNGL
Low energy std Current Curve number
High energy std Unassigned
K factor 1
Time terminator 5.00
(You may change the time after the program starts.
Urines are usually run for 30 minutes.)
Photon monitor ON
H3 range 1-16 KEV

4. Select START COUNTER (#4), and START when ready.

CALCULATIONS

The instrumental printout includes values for counts per minute (cpm), disintegrations per minute (dpm), and efficiency (eff). Concentration is usually determined in dpm, the blank value being subtracted before reporting.

If the value is high enough that dpm isn't calculated by the instrument, manually calculate it as follows:

$$\text{Dpm} = \frac{(\text{Sample cpm}) - (\text{Blank cpm})}{\% \text{ eff}}$$

For liquid samples, convert disintegrations per minute to pCi/ml by multiplying the dpm value by 0.45.

CALIBRATION AND QUALITY CONTROL

1. Approximately every 6 months, analyze 7 working standards in the liquid scintillation spectrometer (Amersham Quenched Tritium Standards, Cat. No. 180070). Correct the tritium

values for decay, using the Universal Decay Table (Table D-1). Store the values as a new calibration curve in the instrument.

2. Maintain the standardization by analyzing a blank and a tritium standard with each set of urine samples.
3. The value of the tritium blank and the efficiency of the tritium standard are tracked on control charts.

REFERENCES

1. F.E. Butler, "Determination of Tritium in Water and Urine," Anal Chem 33:409 (1961).
2. W.H. Langham et al., "Assay of Tritium Activity in Body Fluids with Use of a Liquid Scintillation System," J Lab and Clin Med 47:819 (1956).
3. Mark V Model 5303 Liquid Scintillation Counting System User's Manual, Document No. 710-A50200, Issue B (TM Analytic, 8/1/90).

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TABLE D-1

UNIVERSAL DECAY TABLE ACCESSORIES STATISTICS

A.1 ISOTOPE DECAY TABLES

The Universal Decay Table provides the fraction of activity of a radioisotope remaining, from 0.001 half-life to 1.000 half-life, as calculated from the equation $A/A_0 = e^{-\lambda t} = e^{-0.693t/T_{1/2}}$ where A_0 is the known activity in dpm at a known past date, and A is the unknown present activity. To use this table:

- (1) Determine the half-life of the isotope of interest.

For commonly used isotopes:

<u>ISOTOPE</u>		<u>HALF-LIFE</u>
^3H	-	12.3 years
^{14}C	-	5730 years
^{22}Na	-	2.60 years
^{24}Na	-	15.0 hours
^{32}P	-	14.3 days
^{35}S	-	88 days
^{36}Cl	-	3.1×10^5 years
^{45}Ca	-	165 days
^{60}Co	-	5.26 years

- (2) Divide the elapsed time (t) by half-life ($T_{1/2}$). Time must be in the same units. Enter the table at this ratio to observe the fraction of remaining activity.

- (3) Multiply the original activity by this figure to obtain the present activity.

Example:

Determine the present activity of a ^3H standard that had 250,000 $\pm 3\%$ dpm exactly 1 year ago.

- (1) $t = 1$ year and $T_{1/2} = 12.3$ years, thus $t/T_{1/2} = 0.0813$.

- (2) Entering the table at the 0.080 row and extrapolating between the .001 and .002 columns for the 0.0813 value gives 0.94502 as the fraction remaining.

- (3) Thus, the ^3H standard's current activity is 250,000 (0.94502) = 236,000 $\pm 3\%$ dpm.

UNIVERSAL DECAY TABLE

ACTIVITY REMAINING FOR $t/T_{1/2}$ FROM .001 TO 1.00

	.000	.001	.002	.003	.004	.005	.006	.007	.008	.009
.000	.00000	.99969	.99862	.99793	.99723	.99645	.99586	.99516	.99446	.99379
.010	.99309	.99238	.99172	.99103	.99034	.98966	.98898	.98828	.98759	.98693
.020	.98623	.98554	.98487	.98419	.98350	.98283	.98214	.98146	.98076	.98010
.030	.97942	.97874	.97807	.97740	.97671	.97603	.97517	.97446	.97399	.97333
.040	.97262	.97299	.97132	.97065	.96997	.96930	.96880	.96795	.96726	.96662
.050	.96594	.96527	.96461	.96393	.96326	.96260	.96190	.96125	.96058	.95994
.060	.95928	.95862	.95795	.95728	.95661	.95596	.95529	.95452	.95395	.95331
.070	.95264	.95199	.95133	.95067	.95000	.94936	.94870	.94800	.94738	.94673
.080	.94587	.94522	.94457	.94392	.94326	.94261	.94196	.94130	.94063	.94000
.090	.93926	.93888	.93833	.93759	.93693	.93628	.93564	.93499	.93434	.93370
.100	.93304	.93240	.93175	.93112	.93046	.92982	.92906	.92853	.92887	.92725
.110	.92660	.92596	.92532	.92468	.92403	.92340	.92276	.92216	.92152	.92085
.120	.92020	.91956	.91893	.91785	.91766	.91702	.91639	.91575	.91511	.91446
.130	.91339	.91321	.91265	.91196	.91132	.91069	.91008	.90939	.90841	.90817
.140	.90747	.90691	.90629	.90566	.90502	.90440	.90378	.90314	.90250	.90190
.150	.90127	.90064	.90002	.89931	.89840	.89816	.89754	.89690	.89627	.89566
.160	.89504	.89442	.89381	.89319	.89257	.89195	.89133	.89071	.89008	.88949
.170	.88888	.88825	.88763	.88702	.88650	.88579	.88518	.88456	.88393	.88334
.180	.88272	.88211	.88150	.88098	.88030	.87967	.87905	.87885	.87852	.87724
.190	.87663	.87602	.87542	.87481	.87420	.87320	.87300	.87216	.87178	.87118
.200	.87057	.86997	.86937	.86877	.86816	.86756	.86697	.86636	.86576	.86517
.210	.86456	.86396	.86337	.86277	.86217	.86157	.86082	.86037	.85978	.85919
.220	.85859	.85800	.85741	.85681	.85621	.85579	.85503	.85443	.85384	.85326
.230	.85266	.85207	.85148	.85097	.85030	.84975	.84914	.84853	.84794	.84736
.240	.84677	.84619	.84561	.84502	.84443	.84384	.84326	.84268	.84210	.84152
.250	.84092	.84034	.83976	.83918	.83860	.83802	.83744	.83685	.83628	.83570
.260	.83511	.83454	.83396	.83339	.83283	.83223	.83208	.83166	.83050	.82993
.270	.82935	.82875	.82820	.82763	.82705	.82648	.82591	.82533	.82476	.82419
.280	.82362	.82313	.82248	.82191	.82136	.82077	.82021	.81962	.81907	.81850
.290	.81792	.81736	.81681	.81624	.81567	.81511	.81454	.81397	.81341	.81300
.300	.81228	.81172	.81116	.81060	.81004	.80948	.80892	.80819	.80779	.80702
.310	.80667	.80609	.80556	.80500	.80444	.80489	.80333	.80277	.80222	.80166
.320	.80110	.80055	.80000	.79944	.79888	.79834	.79779	.79731	.79668	.79613
.330	.79557	.79502	.79447	.79392	.79337	.79282	.79227	.79172	.79118	.79063
.340	.79007	.78953	.78899	.78844	.78789	.78735	.78681	.78625	.78571	.78517
.350	.78462	.78408	.78354	.78300	.78245	.78191	.78137	.78082	.78028	.77974
.360	.77920	.77866	.77813	.77759	.77704	.77648	.77597	.77543	.77489	.77436
.370	.77383	.77329	.77275	.77222	.77168	.77115	.77062	.77007	.76953	.76901
.380	.76848	.76795	.76742	.76689	.76635	.76582	.76529	.76476	.76423	.76370
.390	.76317	.76272	.76212	.76159	.76106	.76053	.76001	.75948	.75895	.75843
.400	.75790	.75737	.75685	.75633	.75580	.75528	.75476	.75423	.75371	.75319
.410	.75266	.75215	.75163	.75111	.75058	.75006	.74955	.74902	.74850	.74799
.420	.74747	.74695	.74644	.74592	.74540	.74488	.74437	.74385	.74334	.74282
.430	.74231	.74179	.74128	.74077	.74025	.73974	.73923	.73871	.73820	.73762
.440	.73718	.73667	.73616	.73568	.73514	.73463	.73413	.73361	.73311	.73260
.450	.73208	.73258	.73108	.73057	.73006	.72956	.72958	.72854	.72804	.72754
.460	.72708	.72653	.72603	.72545	.72527	.72452	.72402	.72351	.72302	.72252
.470	.72201	.72151	.72102	.72052	.72001	.71952	.71902	.71852	.71802	.71753
.480	.71702	.71653	.71604	.71554	.71504	.71455	.71405	.71355	.71306	.71257
.490	.71207	.71158	.71109	.71060	.71010	.70961	.70912	.70863	.70814	.70765
.500	.70715	.70666	.70618	.70569	.70520	.70471	.70423	.70373	.70325	.70276

UNIVERSAL DECAY TABLE--Continued

ACTIVITY REMAINING FOR t/T_1 FROM .001 TO 1.00

	.000	.001	.002	.003	.004	.005	.006	.007	.008	.009
.510	.70227	.70179	.70130	.70082	.70033	.69984	.69936	.69887	.69839	.69791
.520	.69742	.69694	.69646	.69598	.69549	.69501	.69453	.69404	.69356	.69309
.530	.69261	.69213	.69165	.69117	.69069	.69021	.68973	.68925	.68877	.68830
.540	.68796	.68735	.68687	.68640	.68593	.68545	.68497	.68450	.68395	.68348
.550	.68307	.68260	.68213	.68166	.68118	.68071	.68024	.67976	.67913	.67882
.560	.66835	.67782	.67742	.67695	.67646	.67601	.67554	.67507	.67461	.67414
.570	.67367	.67320	.67274	.67227	.67181	.67134	.67088	.67041	.66995	.66948
.580	.66902	.66856	.66810	.66764	.66718	.66671	.66624	.66578	.66532	.66486
.590	.66440	.66394	.66348	.66302	.66256	.66210	.66164	.66118	.66053	.66027
.600	.65981	.65935	.65890	.65846	.65798	.65753	.65707	.65661	.65616	.65571
.610	.65525	.65480	.65435	.65390	.65344	.65299	.65244	.65208	.65163	.65118
.620	.65073	.65028	.64983	.64938	.64892	.64848	.64803	.64758	.64713	.64669
.630	.64623	.64598	.64534	.64489	.64448	.64400	.64356	.64310	.64273	.64222
.640	.64178	.64133	.64089	.64044	.64000	.63955	.63911	.63886	.63822	.63778
.650	.63764	.63690	.63646	.63602	.63558	.63514	.63470	.63425	.63382	.63338
.660	.63293	.63250	.63206	.63163	.63118	.63075	.63032	.62987	.62944	.62900
.670	.62856	.62813	.62770	.62727	.62683	.62639	.62588	.62552	.62509	.62466
.680	.62422	.62379	.62336	.62293	.62250	.62207	.62164	.62120	.62077	.62035
.690	.61991	.61936	.61906	.61863	.61820	.61777	.61736	.61691	.61649	.61606
.700	.61563	.61520	.61478	.61436	.61393	.61350	.61308	.61265	.61223	.61181
.710	.61138	.61096	.61054	.61012	.60969	.60927	.60885	.60842	.60800	.60758
.720	.60716	.60674	.60632	.60572	.60548	.60506	.60464	.60422	.60380	.60339
.730	.60296	.60255	.60213	.60172	.60130	.60088	.60047	.60005	.59963	.59922
.740	.59880	.59838	.59797	.59756	.59717	.59673	.59632	.59590	.59549	.59508
.750	.59456	.59426	.59385	.59344	.59302	.59261	.59220	.59179	.59144	.59097
.760	.59053	.59015	.58974	.58934	.58892	.58852	.58811	.58770	.58730	.58690
.770	.58648	.58608	.58567	.58527	.58485	.58477	.58405	.58364	.58324	.58271
.780	.58243	.58202	.58163	.58122	.58082	.58042	.58002	.57961	.57921	.57910
.790	.5784	.57801	.57761	.57721	.57681	.57641	.57601	.57561	.57579	.57438
.800	.57441	.57402	.57362	.57317	.57282	.57243	.57204	.57163	.57124	.57085
.810	.57045	.57005	.56966	.56904	.56856	.56847	.56808	.56768	.56729	.56690
.820	.56645	.56611	.56572	.56533	.56494	.56455	.56416	.56377	.56338	.56299
.830	.56359	.56320	.56282	.56243	.56203	.56165	.56126	.56087	.56049	.56010
.840	.55899	.55837	.55794	.55755	.55716	.55678	.55640	.55601	.55562	.55524
.850	.55485	.55447	.55408	.55370	.55332	.55293	.55255	.55217	.55179	.55140
.860	.55102	.55064	.55026	.54988	.54950	.54912	.54874	.54841	.54797	.54760
.870	.54721	.54683	.54646	.54605	.54565	.54532	.54495	.54457	.54419	.54382
.880	.54344	.54306	.54269	.54231	.54193	.54156	.54118	.54081	.54043	.54006
.890	.53968	.53931	.53894	.53856	.53819	.53782	.53745	.53707	.53670	.53633
.900	.53595	.53558	.53538	.53485	.53447	.53410	.53373	.53336	.53299	.53262
.910	.53225	.53188	.53152	.53115	.53078	.53043	.53005	.52968	.52931	.52895
.920	.52858	.52821	.52785	.52746	.52711	.52675	.52638	.52600	.52566	.52529
.930	.52493	.52456	.52420	.52384	.52347	.52311	.52275	.52239	.52203	.52168
.940	.52130	.52094	.52058	.52022	.51986	.51950	.51916	.51898	.51842	.51806
.950	.51770	.51734	.51698	.51661	.51627	.51591	.51556	.51520	.51484	.51448
.960	.51402	.51377	.51342	.51306	.51270	.51235	.51200	.51164	.51129	.51093
.970	.51057	.51027	.50987	.50952	.50918	.50881	.50846	.50810	.50775	.50740
.980	.50715	.50670	.50635	.50600	.50570	.50535	.50495	.50460	.50426	.50390
.990	.50355	.50320	.50285	.50256	.50216	.50181	.50141	.50111	.50077	.50042
1.000	.50000	.49973	.49938	.49904	.49869	.49838	.49800	.49765	.49731	.49697

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TOTAL URANIUM IN SOIL, URINE, AND WATER

ABSTRACT

A pulsed laser is used to induce phosphorescence from uranium ions, which are complexed with a proprietary complexing agent to produce reasonable decay lifetimes at room temperature. The number of photons detected is proportional to the number of excited ions. Intensity values, taken at fixed intervals, are summed to give good statistics and repeatability.

APPLICATIONS AND LIMITATIONS

The detection limit for the technique is approximately 0.03 ng of uranium. The low range covers the detection limit to >10 ng; high range, 10 ng to 10 µg. Relative standard deviations of 1-2% are common.

ES&H NOTES

The KPA-10 is classified as a Class Ib laser system. The laser is interlocked to turn off when the sample chamber door is opened. Nevertheless, do not open the door while the laser indicator is on to avoid exposing the photomultiplier tubes to excess light.

APPARATUS

Laser phosphorimeter, ChemChek Instruments Model KPA-10

Quartz cells, with Teflon stoppers

Pipets, liquid

Erlenmeyer flasks

Graduated cylinders, 5 or 10 ml

REAGENTS

Laser dye mix - Dissolve 23.9 mg of Stilbene-420 in 25 ml of methanol.

Nitric acid, conc. (70% HNO₃)

Hydrogen peroxide (30%)

Uranium stock standard (1000 µg U/ml) - A commercially-prepared stock standard in nitric acid is used.

Uranium working standards - Prepare working standards of 0.1, 1, and 10 $\mu\text{g/ml}$, acidified to the same strength as the stock standard.

Uraplex complexing agent, available from ChemChek Incorporated

SAMPLE PREPARATION

Water Samples

1. Water samples can be analyzed directly or concentrated by evaporation with 2N HNO_3 to a smaller volume.
2. Pipet 1 ml of water + 1.5 ml of complexing agent into the cell. Insert a clean Teflon stopper into the cell and invert several times to mix, touching only the top and bottom of the cell.

Urine Samples

1. Vigorously shake the urine sample to homogenize, since uranium tends to concentrate in the solids.
2. Digest 5 ml of the homogenized urine in an Erlenmeyer flask with 2 ml of conc. HNO_3 and 0.5 ml of H_2O_2 . Heat, repeating the addition of oxidants 1-2 times as needed, until a pale yellow or white salt forms.
3. Redissolve the salts in a little conc. HNO_3 and deionized water, and dilute to 5 or 10 ml, as desired.
4. Combine 1 ml of the digested sample (NOTE: Avoid pipetting any solids.) with 1.5 ml of complexing agent.

Soil Samples

1. Add a known weight, 5-10 g, of soil to an Erlenmeyer flask.
2. Cover with conc. HNO_3 and H_2O_2 in the ratio 4:1. Digest as in Step 2 under Urine Samples.
3. Add a little conc. HNO_3 and deionized water, filter, and dilute to 5 or 10 ml, as desired.
4. Combine 1 ml of sample with 1.5 ml of complexing agent.

ANALYTICAL PROCEDURE

1. Turn on the KPA and the computer.
2. Prepare the Uraplex complexing agent.

3. Fill the reference cell with a solution of 100-400 ng of uranium in Uraplex to give 20-70 counts/pulse. Place the cell in the right-hand cell holder in the door of the KPA. The reference solution should be replaced approximately monthly (or when the coefficient of linearity value, R^2 , drops below 0.99).
4. Before using any cell, test the background level by running with 1 ml of distilled water + 1.5 ml of complexing agent. The background should be 300 counts or less in the low range and 20 or less in the high range. If it is higher, rinse the cell repeatedly with distilled water and complexing agent until the level is acceptable.
5. When ready to run, insert the cell into the left-hand cell holder in the door of the KPA-10, being careful to avoid breakage or getting fingerprints on it. If you do touch the cell, clean it with methanol; and rinse with distilled water.
6. From the Main Menu, select F5 REFERENCE SOLUTION DATA. Enter the date the reference solution was prepared. The reference solution should be replaced when the lifetime falls below 200 μ s or the R^2 , below 0.99.
7. Select F2 CALIBRATE to access the Calibration Menu, then F1 CALIBRATION. Calibration consists of a background measurement (which is subsequently subtracted from all other measurements) and from 1 to 7 standards per range. Most of our samples are run in the High range, using 3 standards.
  - a. Select the appropriate range using PgUp or PgDn.
  - b. Select F2 EDIT CALIBRATION INFO to enter the standard concentrations and units.
  - c. Fill a rinsed cell with 1 ml of deionized water + 1.5 ml of complexing agent, and insert it into the left-hand cell holder. Select F3 BACKGROUND to run the background measurement.
  - d. Fill a rinsed cell with 1 ml of the first standard + 1.5 ml of complexing agent. Select F1 STANDARD to measure the first standard. Repeat for all standards.
8. Fill a rinsed cell with 1 ml of sample + 1.5 ml of complexing agent.
  - a. Select F1 ANALYZE from the Main Menu to access the Sample Analysis Menu.
  - b. Select F1 ANALYSIS OF SAMPLE, and enter the requested information. Press F1 again when ready to begin the analysis.

- c. The analytical report, displayed after each analysis, may be printed by pressing F2 PRINT REPORT.
- d. Repeat for all samples using F1 ANALYZE NEXT SAMPLE.

REFERENCES

1. Operation and Service Manual for Kinetic Phosphorescence analyzer KPA-10 (Richland, WA: ChemCheck Instruments).

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