FIELD PORTABLE MEASUREMENT OF AIRBORNE BERYLLIUM, CHROMIUM, LEAD AND OTHER METALS: INSTRUMENTS, METHODS AND FUTURE DIRECTIONS

PART II: CHROMIUM, LEAD AND OTHER METALS

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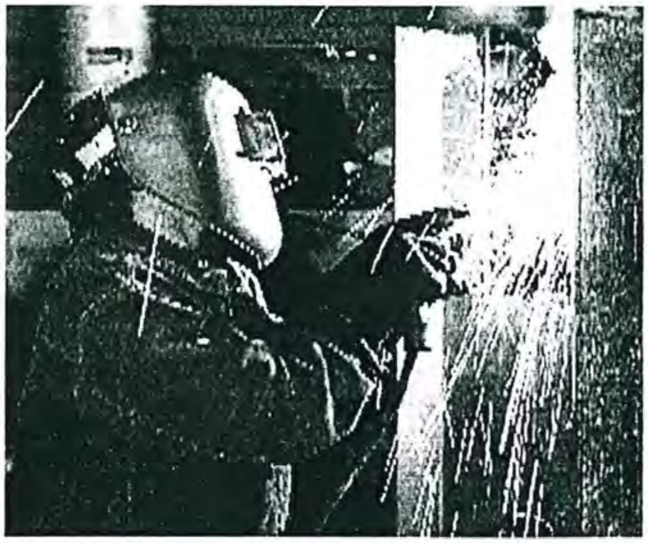

More than 6 million workers in the United States are employed in construction, mining, welding and other occupations that involve metalworking tasks. Variables such as prevailing conditions, the procedure and materials used determine the type, amount and mixture of airborne metals produced. This information along with the worker's time at task is used to assess exposures.

As adverse health effects have been linked to specific airborne metals (see Figure 1), standards based on dust and fume mass per unit volume of air such as the NIOSH recommended exposure limit for welding fume were discontinued. Research efforts at NIOSH are now focused on identifying, characterizing and evaluating portable instruments in order to develop methods for the rapid and reliable measurement of these elements.

Traditionally, workplace samples were sent away to fixed-site laboratories for analysis. In some cases, the analytical results take weeks or even months to arrive. Such delays can compromise worker health if exposures are found to be excessive.

Methods using field portable instruments allow the screening or analysis of samples on location with same-day speed. Samples analyzed nondestructively can be sent for confirmatory analyses if exposures appear to be close to or exceeding the occupational exposure limit. This reduces the number of samples sent to laboratories and makes the exposure assessment process far more cost-effective. Portable methods also facilitate the proper selection and evaluation of exposure controls to reduce the potential for adverse health effects among workers. This article describes the portable X-ray fluorescence (XRF) technologies under evaluation at NIOSH for the measurement of airborne lead and other metals, as well as a need NIOSH method for the measurement of airborne hexavalent chromium.

Figure 1. Example Health Effects From Airborne Elemental Exposures

	As	Be	Cd	Cu	Cr	Mn	Ni	Pb
Metal fume fever				●		●		
Liver damage	●			●	●			
Cancer	●	●	●		●		●	
Respiratory disorders	●	●	●		●		●	
Sinus problems					●			
Parkinson's Disease						●		
CNS disorders	●					●	●	●
Pneumonitis						●	●	
Kidney damage	●		●		●	●		●

Technical Exchange

X-RAY FLUORESCENCE (XRF)

EMERGING PORTABLE TECHNOLOGIES FOR AIRBORNE ELEMENTS

In 1977, a method in the *NIOSH Manual of Analytical Methods* (NMAM) was released for the measurement of silver, cadmium, chromium, copper, iron, nickel, manganese and zinc in welding and brazing fumes on air sample filters by laboratory-grade XRFs. Around this time, battery-powered portable XRFs debuted on the market. Portable XRF quickly found a niche in the rapid measurement of surface lead at Superfund sites. In the mid-1990s, a study found portable XRF to be useful in screening airborne lead samples on mixed cellulose ester filters at a bridge sandblasting operation. This study formed the basis for the 1998 release of NMAM method 7702, Lead by Field Portable XRF. The Health and Safety Laboratory in the United Kingdom also developed comprehensive methods for measuring airborne metals collected on filters using XRF. The HSL methodology was originally written more than two decades ago for full-size laboratory-based XRFs and was revised and expanded to include portable XRF and proficiency test procedures.

The earliest portable XRFs were two-piece units, where the probe and analyzer were connected by a large cable. The typical probes contained one or more sealed radioactive excitation sources; a Mylar-lined probe window where the sample was presented for analysis; and a detector. The analyzer unit contained software for data processing, a keyboard or an array of switches for entering commands and a display to show the analytical results. Most analyzer units also contained rechargeable batteries, which made these units much larger and heavier than similarly equipped new models.

THE 'PERFECT' PORTABLE XRF

The most desirable features in portable XRF instruments are shown in Table I. These features would make portable XRF an indispensable tool for industrial hygienists and occupational safety professionals. While an instrument with all these features is not technologically feasible at this time, XRFs are becoming noticeably smaller and lighter, with lower LODs and improved accuracy and precision. In the mid-1990s, all-in-one instruments were introduced where the probe and analyzer were contained in a single unit, and the first XRF to use a battery-powered X-ray tube became commercially available in 2001. The following sections describe some of the advantages and disadvantages of battery-powered X-ray tube and sealed source XRFs that could influence the buying decision.

RADIOISOTOPE SEALED SOURCE INSTRUMENTS

Radioactive sealed sources are the original excitation sources on portable XRFs. They are the most extensively tested and characterized of all portable XRF technologies. Since sealed sources are natural radiation emitters, they do not require power to operate. Without the need to power the sources, these instruments are generally smaller and lighter than comparable instruments containing battery-powered X-ray tubes.

One potential disadvantage that must be considered in sealed source XRF is the replacement of the radioactive source. All radioactive sources decay with time, resulting in a steady decrease in count rates with a proportional increase in analysis time. Most manufacturers recommend sealed source replacement at approximately 1.5 half-lives to maintain relatively short analysis times and high count rates (Table II). However, such efficiency can be expensive, as replacement costs for a single sealed source can range as high as $5,000. Replacement costs are highly variable and depend on the radioisotope, physical characteristics of the source and the manufacturer. Since more than one isotope may be needed in a portable XRF to analyze samples for multiple metals, the cost of sealed source replacement in the years following instrument purchase could be prohibitive.

The sealed sources used in XRFs emit X-rays at specific energies. Elements that fluoresce at the same or nearly the same energy as the source are either impossible to detect or have very high LODs. For example, cadmium is undetectable on an instrument that uses a cadmium-109 source, and silver, which is a decay product of cadmium, has a very high LOD. In theory, XRFs with cadmium-109 sources are capable of analyzing elements from atomic numbers 22

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Table I. Highly Desirable Features for a Portable XRF Instrument

- LOD < 0.1 PEL for all elements of interest
- Measure as many metals as possible in a single analysis
- Rugged (it works after a rough ride to a work site)
- Resistance to dust, moisture, and electromagnetic interference
- Portable (no larger than a carry-on suitcase)
- Weight ≤ 25 pounds
- Simple, logical operation
- Easy to maintain
- Rapid analysis (results in < 15 minutes/sample)
- Instrument cost ≤ $25,000*

*The desired instrument cost in U.S. dollars was calculated from the laboratory analysis costs for NMAM 7300 (approximately $100 per sample). If 300 samples are analyzed in a year on the portable instrument at a maximum cost of $16 per sample, the instrument would pay for itself by the end of that year.

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through 44 (titanium to ruthenium), and 67 through 94 (holmium to plutonium), although the typical multiple element XRF is not designed to measure more than about 20 elements simultaneously due to potential interferences and other considerations.

In the United States, radioactive sealed sources in XRFs are typically covered by a general license. This license is issued to the instrument manufacturer by the U.S. Nuclear Regulatory Commission and includes rigorous requirements for leak testing, transport, shipping, decommissioning and procedures that must be followed in the event of loss or damage.

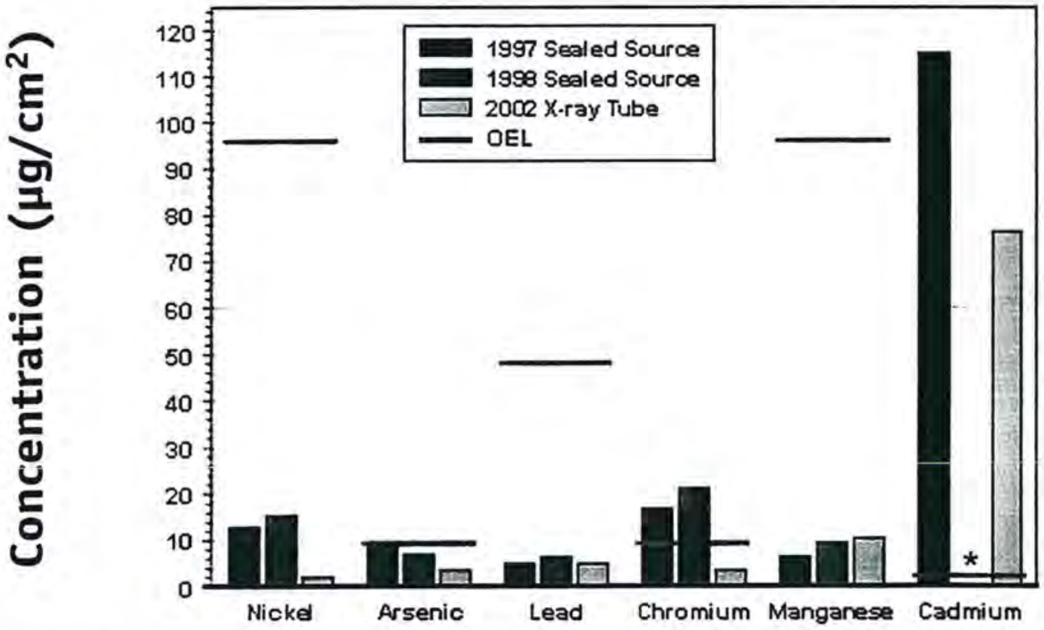
In addition to the above factors, some individuals may simply be uncomfortable with the thought of having radioactive material around. Sometimes, this radiation "mystique" is strong enough to cause the user to shy away from purchasing an XRF with a radioactive sealed source.

BATTERY-POWERED X-RAY TUBE INSTRUMENTS

Portable XRFs that use battery-powered X-ray tubes can measure a range of elements similar to instruments containing cadmium, iron and americium sealed sources. X-ray tubes are not subject to the same rigorous transport, operation and maintenance regulations as sealed sources. Instruments containing X-ray tubes are licensed in the United States by the Food and Drug Administration, so the same regulations that apply to the use and transport of X-ray equipment also apply to XRFs with X-ray tubes. Instrument transport and storage is greatly simplified since radiation is only generated when power is applied. Instruments with X-ray tubes do not show any loss of precision with age, nor do they require adjustments in analysis time to maintain count rates.

The X-ray tubes that were first used in this technology were originally produced for chemotherapy devices. Although the tubes performed well at first, some problems surfaced with use. Imperfections in the tube's glass caused the radiation beam to occasionally drift. Also, the amount of radiation from the tube changed as the anode approached the end of its useful life. In both cases, marked calibration shifts were noted. These problems were apparently eliminated when X-ray tubes were redesigned to specifications made by the XRF manufacturer. Most of the earliest instruments have had the new tubes installed. Instruments currently in production use these improved tubes.

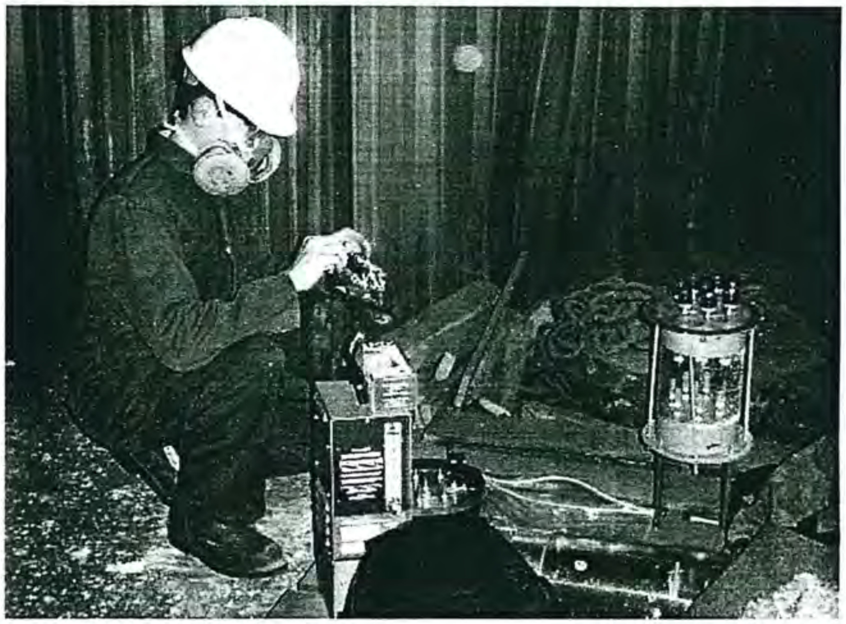
Figure 2. Limits of Detection (LOD) by Instrument



LOD values are based on 180 second analysis times.

All values are in µg/sample and are based on an 8 hour sample with a flow rate of 2L/min, yielding a total sample volume of 0.96 cubic meters.

***Instrument unable to detect this element.**



The major drawback of portable X-ray tube XRFs is the large current drain the tube places on the battery. If a single battery is used, it must power the electronics and other functions of the instrument and must be recharged more frequently than an equivalent instrument containing a sealed source. Some manufacturers have configured the instrument's power supply so the X-ray tube is powered by a separate battery. Even in this case, the battery-powering the X-ray tube only has a life of about four hours of continuous use on a full charge. As the rechargeable battery technology improves and battery-powered X-ray tubes become more efficient, the frequency of battery recharging and replacement will decrease. Most manufacturers now offer a battery replacement unit that allows the X-ray tube to be operated on household current. This is a good solution for locations where household current is nearby. Unfortunately, this is not the case in some workplaces such as mines.

A common misunderstanding of battery-powered X-ray tube XRFs is that the tubes never need to be replaced. The components of the X-ray tube are subject to heat stress, and these parts fail in much the same way as incandescent light bulbs or vacuum tubes. Unfortunately, this typically occurs without warning. Typical X-ray tubes in laboratory-grade XRFs have a lifespan of three to four years. The battery-powered X-ray tube in one of the first portable XRFs to be tested at NIOSH was operated for more than 2,000 analysis hours before it failed. If this is indeed the average lifespan, then these X-ray tubes will have a useful life that rivals those in conventional laboratory XRFs. A better estimate of the lifespan will be known as more instruments are sold and a more extensive maintenance record is established.

A major drawback to X-ray tube replacement is that it requires returning the instrument to the factory. One way to avoid unexpected downtime is to have an identical tube or filament built into the instrument that can be activated by the user until a convenient time is reached for servicing. Unfortunately, this option does not yet exist on these instruments.

A new battery-powered cold cathode X-ray tube was recently produced in the United States. The manufacturer claims that this tube uses stronger materials at key parts, making it more durable and capable of producing X-rays

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Table II. Half-Lives and Recommended Replacement Times for Some of the More Common Sealed Sources Used in Portable XRFs

Radioisotope (element name–isotope)	Half-Life (days)	Recommended Replacement
^{153}Gd (gadolinium-153)	241	annual
^{57}Co (cobalt-57)	271	annual
^{55}Fe (iron-55)	983	5 years
^{241}Am (americium-241)	158,153	600 years
^{109}Cd (cadmium-109)	453	2.5 years

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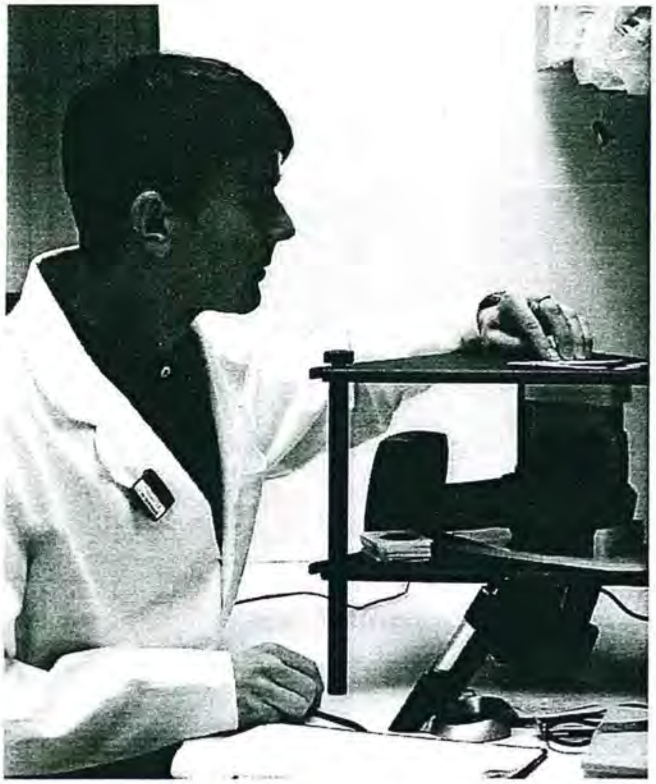

with less battery drain than the traditional silver anode tube. This technology is presently in limited use for alloy and soil testing, and its utility in measuring airborne metals collected on filters has not been demonstrated. If this tube is indeed proven to be useful for filter analysis, the battery-powered X-ray tube lifespan could be extended and operating costs for this technology may decrease.

As was the case with sealed radioactive sources, the XRFs with battery-powered X-ray tubes have "blind spots" for elements with fluorescence energies at or near the excitation energy of the material used to generate the X-rays. For instance, instruments containing conventional silver anode X-ray tubes have difficulty detecting silver and other elements with fluorescence energies that are nearly the same, such as cadmium. Portable battery-powered XRFs containing a secondary anode composed of a different material such as tungsten may eliminate this problem. However, a battery-powered XRF containing either two X-ray tubes or a single X-ray tube with dual anodes has not been produced.

Other drawbacks of the X-ray tube instruments are their bulk and weight when compared with units containing radioactive sealed sources. This is largely due to the amount of battery power needed to operate them. Finally, the ruggedness of these instruments through periods of frequent travel is largely untested, although the instrument under evaluation at NIOSH has performed well during a large worksite survey in 2003.

RADIATION SAFETY

Sealed sources contained in portable XRFs have shielding around the radioisotopes to protect the user and those nearby from radiation. X-ray tubes are designed to emit radiation in a highly directional pattern only when the unit is on, so XRFs with this technology do not require the same radiation shielding as sealed source instruments. However, manufacturers of all portable XRFs advise operators to wear radiation dosimeters and to exercise proper care when operating these instruments. To confirm radiation doses, a secondary dosimeter for the user such as a ring badge is recommended. Since 1997, of all dosimeters worn by scientists operating portable XRFs at NIOSH, only one reported a level of radiation that was above detection. The level measured was well below the threshold limit value, and a

Table III. Relative Extraction Recoveries of Chromates (Cr6+) by Condition (Key: 0 = less than 0.1 percent, ++++ = 84–108 percent)

Conditions	Soluble	Sparingly Soluble	Insoluble
Sulfate and Hotplate	++++	++++	0
Carbonate and Hotplate	++++	++++	++++
Sulfate and Ultrasonic	++++	++++	0
Carbonate and Ultrasonic	++++	++++	++++

subsequent investigation determined that at the badge was placed near a conventional computer monitor for several nights when it was not in use.

LIMITS OF DETECTION

The LODs of two portable sealed source XRFs (manufactured in 1997 and 1998) and a newer silver anode battery-powered X-ray tube XRF (manufactured in 2002) were recently compared at NIOSH. The LODs for some elements of health concern (a few of which are shown in Figure 2) approached one-tenth of the occupational exposure limit for the instrument manufactured in 2002 (defined as the lowest of the ACGIH TLV®, NIOSH REL and OSHA permissible exposure limit for each airborne element when collected for eight hours at 2 L/min). This is a sharp contrast to the models manufactured four and five years earlier. The X-ray tube XRF had lower LODs than the sealed source instruments for arsenic, cadmium, chromium and nickel, and similar performance for lead and manganese. The observed differences were likely the result of improved detector technology in the newest instrument.

The instrument containing the single cadmium-109 sealed source could not measure cadmium. Although the second sealed source model used a different radioisotope to measure cadmium, the LOD was still unacceptably high and well above the OEL. The LOD for cadmium on the X-ray tube instrument was also unacceptably high (see explanation above).

The use of elements other than silver in the construction of battery-powered X-ray tubes (such as tungsten) should result in a radical decrease in silver and cadmium LODs. A battery-powered instrument containing a tungsten anode tube will be characterized and evaluated at NIOSH during 2005.

ACCURACY

Chromium, nickel, iron, copper, manganese, lead and zinc standards (Mylar-based, certified concentrations) in at least three concentration ranges were measured under identical conditions (five measurements each at 180 seconds) on the three instruments used in the LOD study just described. Bias, precision and accuracy were calculated using NIOSH protocol. Although zinc, chromium and iron did not completely meet the NIOSH 25 percent accuracy criterion on the oldest sealed source XRF, all elements were well within the accuracy criterion for the newer sealed source and X-ray tube models. Improved technology appears to be mainly responsible for the improved accuracy. Longer measuring times and additional technology improvements are expected to further improve accuracy.

FUTURE RESEARCH DIRECTIONS AT NIOSH FOR PORTABLE XRF

A series of detailed characterization and performance studies are under way to evaluate additional portable XRFs. The instruments that are successfully characterized in this phase will be used to analyze hundreds of fume and airborne metal samples from experimental and workplace sources, with the results compared against confirmatory analysis at an off-site laboratory. Elements that are successfully measured in workplace settings will form the basis for expanding NIOSH methodology for portable XRFs to include additional elements and portable technologies.

CHROMIUM

CHEMISTRY, HEALTH AND REGULATIONS

Chromium occurs primarily in trivalent and hexavalent states, and there is a long history of adverse health effects to chromates among exposed workers in industry. In recent

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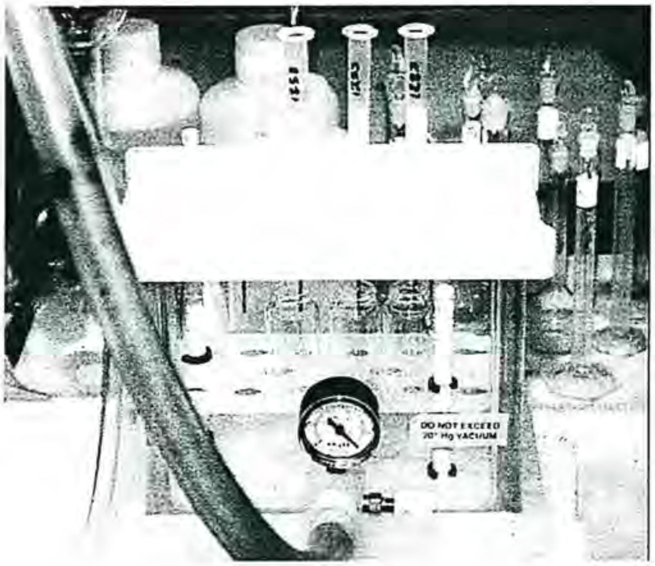
Table IV. NMAM Method 7703: Hexavalent Chromium by Anion Exchange and Portable Spectrophotometry

Limit of detection	0.08 µg per sample
Limit of quantitation	0.27 µg per sample
Bias	-1.0 percent
Overall precision	0.080
Range	1–400 µg per sample
Accuracy	± 15.7 percent
Interferants	Magnesium (Mg), Mercury (Hg), Iron (Fe)

(Continued from p. 59)

years, the technologies for measuring the species of chromium responsible for adverse health effects have radically improved to the point that a NIOSH field portable method for measuring hexavalent chromium (chromates) in workplace air samples could be developed.

Chromium metal is arrived at by refining and is present in many alloys. The trivalent (3+) state of chromium is found naturally in chromite ores. Bivalent (2+) chromium is used in industry to make electronic products and semiconductors. Quadrivalent (4+) and pentavalent (5+) states are highly unstable. The hexavalent (6+, chromate) state is almost entirely anthropogenic and has been used widely in industry. Chromates have been used in a wide variety of anticorrosion agents. Water-soluble chromates have been used in processes such as electroplating, pigments, dyes, tanning and wood treatment. Sparingly soluble and insoluble chromates have been used in pigments, varnishes, rubber and printing. Chromates are also found in stainless steel production and welding.



As useful as chromates are, they are also acidic, oxidizing and highly toxic. Inhalation exposures to soluble and insoluble chromates have been shown to be genotoxic and carcinogenic, with lung cancer as the common endpoint. Water-insoluble compounds are actually soluble in biological systems since they are fat-soluble and can penetrate the thin membranes that line the skin, eyes, nasal passages, lungs, mouth and gastrointestinal tract. Water-soluble chromates are associated with ulceration and perforation of the nasal septum, necrosis, emphysema, inflammation and respiratory cell damage. Dermal contact with chromates can cause allergic reactions and dermal ulceration.

Recently, ACGIH has established separate TLVs for soluble and insoluble chromates. Therefore, a portable method that can separate and measure the amounts of these chromate species would be highly desirable. Also, OSHA has proposed a new PEL for chromates that is much lower than the current PEL. Hence, highly sensitive measurement methods are required for chromates.

Traditionally, air sampling for metals involved the use of filters contained in closed-face cassettes. Unfortunately, mixed cellulose ester filter media can react with chromates and cause reduction, giving artificially low chromate readings. Other factors that can cause chromate reduction include divalent (2+) iron, acids and organic compounds. In an attempt to eliminate potential chromate reduction, a method developed in the United Kingdom recommends treating the filter with base to help stabilize the sample when measuring highly acidic aerosols. In the United States, impingers and/or bubblers are often used in series. They are excellent for area sampling of highly reactive chromate aerosols but not very practical for personal sampling.

HISTORICAL BACKGROUND AND METHOD DEVELOPMENT

In sampling and analysis of chromium compounds, there is great concern with redox chemistry. Specifically, attention is drawn closely to the oxidation of trivalent chromium and the reduction of hexavalent chromium. Depending on the nature of sampling and analysis, different analytical paths must be used.

Various media have been proposed for the dissolution of soluble Cr(VI) compounds. Solutions of varying pH and/or complexing ability have been investigated. The historical development of sample preparation for measuring soluble chromates began in 1979 when Thomsen and Stern used ordinary water. This is simple and preferable in theory, but water has no buffer capacity and therefore results are difficult to reproduce. In 1983, Blomquist and colleagues used acetate buffer. The following year, Zatka reported using dilute sulfuric acid and sodium carbonate in separate studies. While these dissolve soluble and sparingly soluble forms, they have the undesired potential of dissolving the insoluble compounds. The use of ammonium sulfate buffer, first reported by Wang and colleagues in 1997, was a breakthrough in that it appeared to be selective in dissolving only the soluble and sparingly soluble chromate compounds.

A number of procedures have been used for the preparation of samples containing insoluble chromates. In 1974, Abell and Carlberg reported using hot plate extraction with sodium carbonate/bicarbonate buffer. Although this worked well for dissolving insoluble chromates, higher strength buffers are recommended by OSHA for especially stubborn chromate compounds that are difficult to put into solution. Nearly two decades later, a German group (BIA) reported success when using phosphate buffer in place of the carbonate/bicarbonate buffer. Toward the turn of the century, a team led by Ashley found that ultrasonic extraction could be used instead of hot plate digestion for effective extraction of soluble and sparingly soluble chromates. At about the same time, a group in the United Kingdom found ultrasonic extraction to work well for insoluble chromate compounds as well. Ultrasonic extraction can be performed far more easily and safely on location than can hotplate digestion.

METHOD PERFORMANCE

When soluble, insoluble and sparingly soluble chromate compounds were extracted using hotplate or microwave digestion with either a mixture of ammonium sulfate and ammonium hydroxide or sodium carbonate and sodium hydroxide, good recoveries were noted in every case except for the two instances where insoluble chromate was treated with sulfate buffer, in which case there was no detectable recovery (Table III). As a result, the NIOSH method for field portable measurement of insoluble chromates was modified so that carbonate buffer and ultrasonic extraction were used to extract insoluble or total chromates.

Following extraction, the chromates (6+) are separated and isolated from trivalent (3+) chromium and other metals and elements that may be present in the extract. This is accomplished fairly easily since chromate is anionic, or negatively charged, in basic solutions, while trivalent chromium and other metal species are positively charged, or cationic. The separation is done using a process known as anion-exchange solid-phase extraction. Chemically similar to ion chromatography, anion-exchange SPE is portable and has been used with success on location in the field. The device contains an anion-exchange resin in a SPE cartridge. When a vacuum is applied to the cartridge, the liquid sample is drawn in. Chromate is bound to the resin within the cartridge, while the other metals and elements remain in solution and pass through. The chromate is subsequently chemically removed (eluted) from the cartridge and then reacted with a solution containing 1,5-diphenyl carbazide to produce a large molecule known as a chromous complex. The chromous complex has a characteristic bright magenta color in the visible portion of the spectrum, which is identified and quantified using a portable battery-powered spectrophotometer.

This portable method was recently released in the *NIOSH Manual of Analytical Methods* as NMAM 7703. The method has also been patented (U.S. Patent 6,808,931). Figures of merit for this method, which are comparable with similar laboratory-based methods, are shown in Table IV.

Method evaluation studies found recoveries from PVC filters to range from 93 to 98 percent for chromates and 97 to 113 percent for total chromium (all valence states). Recoveries from mixed cellulose ester and polyvinyl chloride filters spiked with chromate in concentrations around the ACGIH TLV, along with trivalent chromium and divalent iron, found that trivalent chromium did not interfere with chromate analysis. However, divalent iron interfered with chromate detection. Results were essentially the same for both filter media.

NIOSH Method 7703 allows soluble chromate compounds to be extracted and measured. Sparingly soluble chromates are also extracted when a sulfate buffer is used. A carbonate buffer is used for the extraction and measurement of insoluble or total chromates. The portable battery-powered spectrophotometers used in this method were very basic in design. The least expensive instruments are in the $2,000 range. ◇

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The information in this article was based on two presentations which were made in roundtable session 214 (Field Portable Measurement of Airborne Beryllium, Chromium, Lead and Other Metals: Instruments, Methods and Future Directions) presented at AIHce 2004 in Atlanta: (1) "Emerging Portable X-Ray Fluorescence Technologies for Measuring Airborne Arsenic, Cadmium, Manganese and Other Metals" by Nicholas J. Lawryk of the NIOSH Health Effects Laboratory Division; and (2) "NIOSH Field Method for the Determination of Hexavalent Chromium in Workplace Air" by Kevin E. Ashley of the NIOSH Division of Applied Research and Technology and Pamela L. Drake of the NIOSH Spokane Research Laboratory. The session was arranged by Nicholas J. Lawryk and sponsored by the AIHA Aerosol Technology Committee.

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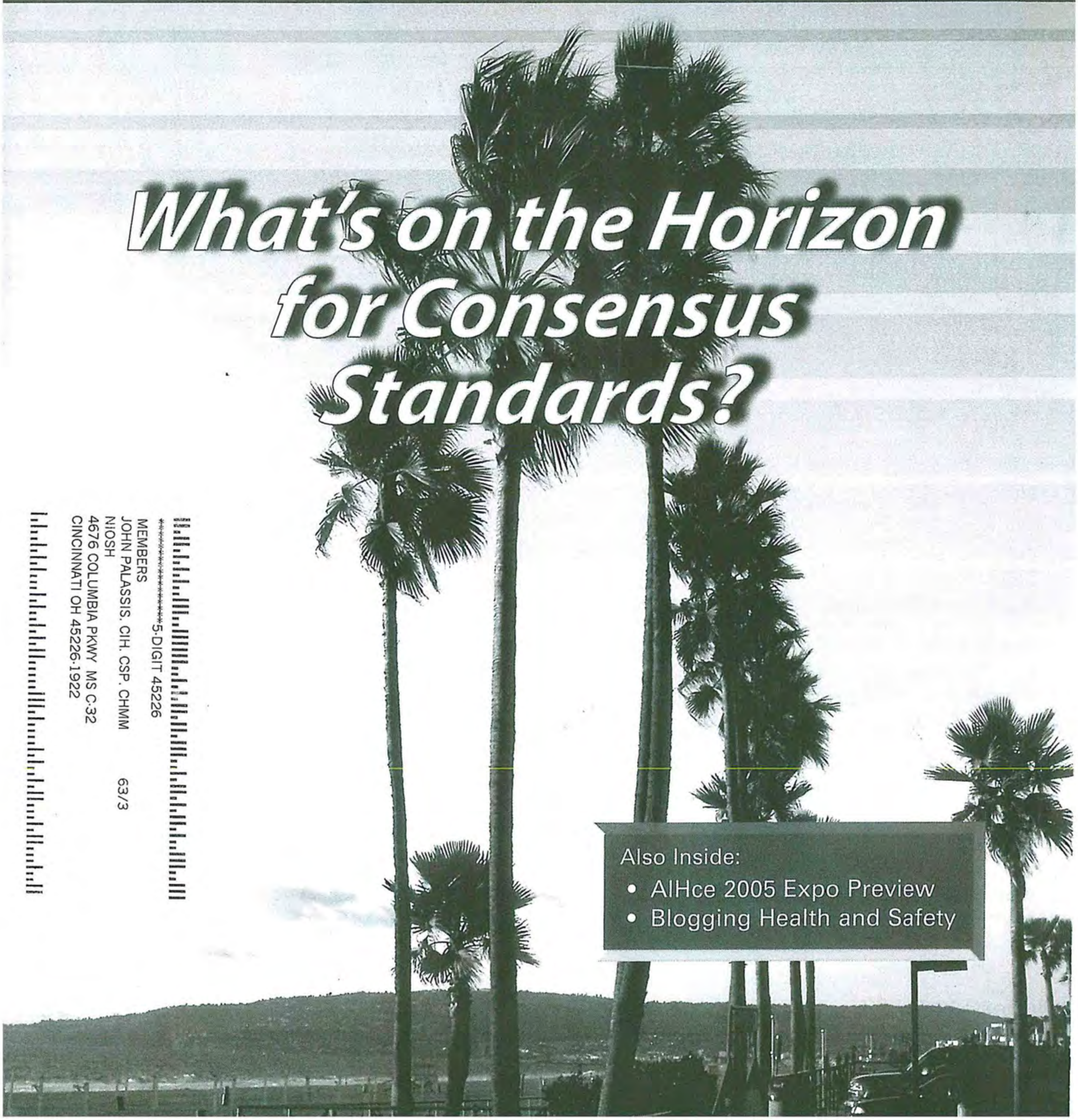

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