



## Technical Exchange

# FIELD PORTABLE MEASUREMENT OF AIRBORNE BERYLLIUM, CHROMIUM, LEAD AND OTHER METALS

INSTRUMENTS, METHODS AND FUTURE DIRECTIONS

## PART I: BERYLLIUM

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Beryllium is one of the lightest, strongest and hardest metals known, with remarkable resistance to deformity over a wide range of temperatures. These properties make beryllium ideal for aerospace and military applications. Beryllium is used in a wide range of products, including weaponry, nuclear reactors, x-ray windows, space optics, missile fuel and space vehicles. Beryllium oxide is used as an electrical insulator and heat conductor. Copper and beryllium are often blended to form an alloy that is an excellent conductor of electricity and heat, resistant to corrosion, nonmagnetic and far stronger than copper alone. Beryllium may be found at a variety of sites, ranging from the deactivation and decommissioning of facilities where beryllium-containing items were produced, stored and tested, to machine shops, ore extraction plants, ceramic plants and beryllium alloy manufacturers. The United States supplies most of the world with beryllium products and is one of only three countries that process beryllium concentrates and ores.

Along with the remarkable properties of beryllium are its toxicity and potential carcinogenicity. Chemical pneumonitis is the primary acute effect of airborne beryllium exposure. Chronic effects include hypersensitivity reactions, immune responses and lung cancer.

In the workplace, airborne beryllium exposures are often first thought of in terms of inhalation at the source of the dusts or fumes. With time, the dusts and fumes settle on surfaces, and the potential for exposures by dermal and ingestion routes increases. These exposures may occur very far from the source since beryllium may be transported on items such as tools, footwear and clothing.

Portable technologies that rapidly identify and measure surface and airborne concentrations of beryllium on location can be of great value in the selection and evaluation of engineering controls and personal protective equipment to minimize exposures and potential adverse health effects.



However, these technologies have yet to meet with full success. Recently, the U.S. Department of Energy (DOE) and NIOSH have worked to encourage scientists in government and industrial sectors to develop and find ways to validate these instruments. This report explains the quest for portable technologies to measure airborne and surface beryllium, the problems that must be addressed in the characterization of these technologies and the development of methods for successfully applying these technologies to assess exposures where they may be occurring.

## WHY BERYLLIUM?

Airborne beryllium exposures are associated with an immune disease that impacts lung tissue known as berylliosis or chronic beryllium disease. Since extremely low concentrations of airborne beryllium can cause CBD, the DOE developed the Chronic Beryllium Disease Prevention Program Rule, 10 CFR Part 850 (henceforth referred to as the "Rule"). Introduced in 1999, the Rule requires surface and air monitoring for beryllium to determine health risks and the effectiveness of control measures intended to reduce or eliminate those risks. The Rule includes an action level of  $0.2 \mu\text{g}/\text{m}^3$ . Like the OSHA permissible exposure limit, the Rule uses this limit as an "action level" where protective

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procedures, guidelines and requirements are activated to protect all workers potentially exposed to beryllium. Additional studies have suggested that dermal exposures to beryllium dust may also sensitize workers so they are more likely to develop CBD than those who were not exposed. Although the dermal exposure issue was not the basis for the DOE beryllium surface contamination limit, the surface limit has become important since there may be skin exposures wherever fine beryllium particles are found in the air. The prevalence of beryllium in certain work sites and its association with adverse health effects at low concentrations prompted the search for portable instruments and methods that could rapidly measure beryllium on air sample media and in surface dust. The DOE has a surface limit of  $3 \mu\text{g}/100 \text{ cm}^2$  for beryllium areas and  $0.2 \mu\text{g}/100 \text{ cm}^2$  for release of equipment that was in a beryllium area. To date, the DOE has not developed a standard for legacy areas or non-beryllium areas. If NIOSH adopts a different posture on surface limits, especially if it is based on health risks due to dermal exposures, it is logical that the DOE would adopt this standard.

For decades, scientists have been unable to find a sensible exposure-disease connection for beryllium. In addition to dermal exposures, bioavailability factors such as particle size, number and surface area may play a major role in the development of CBD in exposed workers. This makes sense because CBD is an immune disease. When particles are inhaled, some settle out in the alveoli, the deepest portions of the lungs where gas exchange takes place. Like other organs in the body that interface with the environment or bloodstream, alveoli are protected by large white blood cells known as macrophages. The macrophages are scavengers, engulfing and chemically destroying (lysing) microbes, antigens and other foreign matter they encounter on the alveolar surfaces. Unfortunately, the body's inflammatory efforts to protect itself from beryllium create granulomas, or scars, in the lung tissue. As the number and coverage of granulomas increase, the efficiency of gas exchange in the lung is reduced.

Studies have shown that different manufacturing operations have different particle size distributions. Some operations have very high concentrations of beryllium particles in the ultrafine region (those with a diameter smaller than  $0.5 \mu\text{m}$  that can be deposited in the alveoli). Since factors associated with the bioavailability of inhaled beryllium may be more important contributors to increased CBD risks among exposed workers than airborne beryllium mass-based concentration and time at task, the focus of future research must shift to quantifying these factors, which should, in turn, provide a more accurate indication of CBD risk among workers exposed to beryllium.

The main objective of rapid portable beryllium monitoring is to improve the margin of safety and protection for workers through timely feedback of exposure information. Portable instruments facilitate quick and more effective use of exposure control measures by identifying the areas and processes with high beryllium concentrations. Portable instruments capable of rapidly measuring surface beryllium could also be used to check for contamination on tools and other items regularly moved into and out of beryllium-containing sites. In deactivating and decommissioning operations, the level of personal protective equipment is typically increased to excessive levels, since it is best to overprotect the worker in areas where beryllium concentrations are unknown. Rapid portable monitoring will allow PPE adjustments to be made, avoiding the expense of overprotection and improving worker productivity. Since portable monitoring methods typically use less expensive analytical or screening technologies, more samples can be collected around a work site, allowing excessive beryllium exposures to be easily identified. In previous years at large research facilities such as Los Alamos National Laboratory (LANL), many scientists have conducted independent studies, and records of beryllium use and disposal may not have been properly maintained. Rapid portable monitoring can effectively and quickly identify and evaluate pockets of beryllium contamination in these legacy areas that may otherwise go undetected.



## TECHNOLOGIES FOR BERYLLIUM MEASUREMENT IN AIR AND DUST

The present standard method for measuring beryllium in air involves sample collection on conventional closed-face cassettes measuring 37 mm in diameter. The sample filters are then sent to a laboratory where they are chemically digested and suspended in solution. The solution is then analyzed by inductively coupled plasma. The ICP method has a low limit of detection and is very accurate. Unfortunately, the laboratory instruments used for this method are far from portable. Also, depending on the laboratory, weeks may pass from the time the sample is sent to the time results are received. With an average analysis cost of approximately \$100 per sample, the investigator finds that the number of samples taken is affected by the cost, which discourages one from collecting the number of samples needed to decisively locate and quantify beryllium contamination sources.

A symposium entitled "Beryllium Particulates and Their Detection" was held in February 2002 by a network of senior scientists and engineers from DOE and LANL to search for portable monitors capable of rapidly measuring airborne and surface beryllium. The Beryllium Advanced

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Technology Assessment Team was formed as a result of this symposium. The team, consisting of scientists from NIOSH, OSHA, DoD and DOE, sought to identify and develop portable instruments for rapid detection of beryllium in the workplace. Although the team accomplished its mission of identifying a variety of suitable technologies and was subsequently disbanded, the Beryllium Health and Safety Committee formed a new subcommittee to pursue ongoing beryllium sampling and analytical issues.

One of the most extensively tested portable technologies for measuring airborne beryllium on location uses laser induced breakdown spectroscopy. At its heart, the LIBS technology has a laser that is focused into a spark. Beryllium and all other elements passing the spark become plasma in the airstream as electrons go from lower energy inner shells to higher energy outer shells. When the elements return to their normal ground states, they produce a spectral signature of visible, infrared and ultraviolet energies. The LIBS instrument contains a spectrograph, detector and computer that reads these energies and reports the type and amount of each element present.

LIBS technology has been successfully used at the DOE to determine high airborne concentrations of beryllium in plasma spray operations. The LIBS instrument that was used in this trial measured air samples at 30-second intervals, and a separate chart showed the integrated (overall) concentration values. Although short sampling intervals are highly desirable, they come at the expense of a higher LOD than the ICP laboratory method. Depending on intended use and analytical requirements, LIBS instruments can be as small as a shoebox. However, most instruments are large, ranging up to the size and weight of a full-size refrigerator. For this reason, the technology is generally referred to as "field-transportable" rather than portable.

In general, the other instruments for detecting beryllium in air samples and on surfaces were large in size, with the smallest instruments being about the size of a carry-on suitcase. Some instruments had very novel and interesting features, such as one LIBS unit that was robotic. The instrument collected air on a filter and then automatically transferred it to a section where it was analyzed and the amount of beryllium was reported. Although the LOD was  $\sim 0.06 \mu\text{g}$  per sample, the instrument was slightly smaller than a free-standing kitchen refrigerator. However, it could be rolled about on a set of built-in castors.

Another LIBS instrument used an aerosol focusing technology. The instrument collected the air sample, a particle beam was focused on the sample and a spectrometer reported the amounts of beryllium and other metals. This prototype unit is comparatively small, about the size of a window air conditioner.

Other LIBS instruments for measuring beryllium and other metals on surfaces and in soil are as small as a catalog

case. Since they are battery powered, they can provide rapid concentration readings on location in the workplace. However, the size of the LIBS instrument is inversely related to the LOD (the smaller the instrument, the greater the LOD).

Some technologies use a technique known as microwave induced plasma spectroscopy. Like LIBS, there is a similar principle of turning airborne elements into plasma, but this is accomplished by using microwave energy instead of a laser. The current commercially produced MIPS instrument is very expensive (about \$85,000 to \$350,000). However, the more expensive instrument has an extraordinarily large sample and plasma volume, which means more beryllium particles can be detected per unit sample, driving the LOD to levels below those of LIBS technologies. Although this MIPS instrument with the low LOD is very large, a smaller instrument has been developed with a far smaller plasma volume. At present, this instrument is in the prototype stage and is now becoming commercially available.

Adsorptive stripping voltammetry (AdSV) is another portable technology that shows promise for rapid analysis of beryllium on site. A sample is placed in the top of the instrument, where the medium is digested. The sample is extracted through treatment with an acidic solution and ultrasound. A chemical reaction combines any beryllium with a carbon-containing (organic) molecule known as a ligand. The beryllium-ligand complex removes (adsorbs) light of a certain wavelength when light of a full range of wavelengths is directed at the solution containing this complex. Special detectors called fluorimeters can detect this "hole" in the spectrum, allowing one to positively identify beryllium in the sample. AdSV then determines the amount of beryllium in the sample. The instrument is about the size of two shoeboxes put together, making it more portable than most technologies evaluated, and it weighs less than 10 kg. Although the cost of the instrument is around \$15,000, the manufacturer has judiciously elected not to sell the instrument at this time since they felt it needed further evaluation.

Another technology that has been used for detecting and quantifying airborne beryllium and other metals, elements and substances is aerosol time of flight mass spectrometry. This instrument is among the most complex of the portable instruments, and it generates an amazing amount of information on each air sample it collects. When the instrument draws air in, airborne particles are initially slowed and then accelerated into a chamber. The particles then pass into a mass spectrometer and a laser and electric fields are used to ionize and accelerate the particles before they strike an ion detector, which determines additional characteristics such as chemical composition and form (oxide, silicate, salt, sulfate, organic, etc.). In addition to beryllium, the instrument can be tuned to detect a variety of elements and metals, including fluorine, magnesium,



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zinc and chromium. In addition to airborne particle composition, concentrations of the collected components are reported by this instrument. The wealth of information comes at a price, however, as it is housed in a large cabinet that occupies slightly more than 1.6 m<sup>3</sup> and weighs about as much as a well-stocked household refrigerator (360 kg). The current price is approximately \$400,000.

Colorimetric analysis is one of the most inexpensive and simple of all portable methods available for rapid beryllium measurement. Colorimetric methods are popular in developing countries such as Kazakhstan, where they have been used to determine residual skin contamination among plant workers. The inner wrists of workers are swabbed after they have taken their mandatory shower following their shift. The swab is immediately processed using a set of reagents. Resulting color levels correspond to beryllium concentration on the swab and, in turn, the skin. Workers showing any measurable beryllium on their skin must return to the showers. This method has also been developed into a wet chemistry method with a beryllium LOD in the range of 5 parts per billion. Fluorometric methods similar to these colorimetric methods also exist. Kazakhstan uses one of these methods as a standard in place of ICP. In the United States, a wet-chemistry fluorometric method has been developed from this technique and is currently being tested by NIOSH for possible inclusion in the next edition of the *NIOSH Manual of Analytical Methods*.

The statuses of the portable beryllium measuring technologies evaluated by the DOE are summarized in Figure 1. Some are in the technology development stage, some are in

Table I. Wish List of Criteria for the "Perfect" Beryllium Monitor

- Measure in real-time or provide end-of-shift results (at least)
- The LOD is no greater than 10 ng
- Distinguish natural and man-made beryllium
- Identify chemical form(s) of beryllium
- Analyze samples nondestructively (allowing confirmatory analysis)
- Characterize airborne beryllium particles (number, surface area and size)
- Small enough to be used on a worker for collecting breathing zone samples
- Cost-effective to buy and use (under \$25k)
- Rugged (can operate even after a rough ride to the workplace)
- Validated in both laboratory and workplace
- Proven ability to assess beryllium exposure risk

instrument that has all of these features is probably decades away from becoming a reality. However, occupational health and safety professionals must realize that instruments that are successful at achieving even a few of these characteristics could be highly useful. For instance, screening methods can determine which samples are positive for beryllium and require further analysis, thereby greatly reducing the number of samples that must be sent to the laboratory for more costly quantitative analysis. Provided the up-front and sample analysis costs are reasonable, a screening method that allows efficient sample selection for qualitative analysis can rapidly pinpoint exposures and greatly reduce overall analytical expenses.

## FUTURE DIRECTIONS

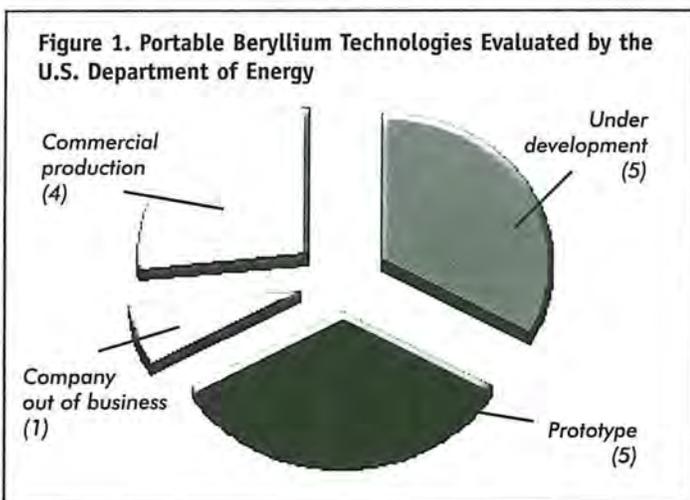
In order to develop the appropriate portable instruments and methods and get them out to the workplaces where they are needed, a beryllium aerosol laboratory must be developed for instrument evaluation and validation. In addition, instrument criteria and validation procedures must be developed and closely followed. Once this stage is reached, three or four technologies that show the strongest potential can be selected to go forward for final development.

Beryllium sensitization and disease does not follow a simple dose-response relationship and may depend on factors such as particle size and number. Consequently, particle number may be a good metric for inhalation exposure risk. Since dermal contact may be a route of sensitization, there is also a need to investigate and validate portable methods for surface sampling to properly assess beryllium exposures.

## A REAL-LIFE EXAMPLE OF REAL-TIME MONITORING

A prototype LIBS surface sampler with a "point and shoot" design was used in a recent study to determine the

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the prototype stage. None of the instruments have been validated yet. It is important for manufacturers to find ways to get these instruments into production so cost and time can be reduced for analysis and effective exposure controls can be implemented where they are most needed.

The characteristics of the ideal beryllium monitor are listed in Table I. Given the characteristics of currently available beryllium monitors intended for portable use, an

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presence of beryllium on clothing, tools, air sample filters, dust samples from vacuum cleaner bags and wipe samples from various surfaces such as carpets and upholstery. As a screening-type technology, the LIBS instrument allowed the investigators to determine which samples needed to be sent to an off-site laboratory for quantitative confirmatory analysis. In this respect, the technology saved both money and time. However, the instrument was expensive and not widely available. It would be highly desirable if the portable LIBS technology were inexpensive and widely available. Instruments used in beryllium-containing areas often have to be dedicated for this purpose, since it is almost impossible to clean most instruments used in beryllium-contaminated environments to background levels.

Characterization studies of LIBS found that instrument response was not always proportional to the size of the beryllium particles measured. Possible reasons why this was happening include: (1) some particles were not directly in the center of the laser, and only partially turned to plasma; (2) the interior of larger particles was not penetrated by the laser and vaporized; and (3) multiple species of beryllium with different vaporization energies (such as oxides and alloys) may have been present with metallic beryllium. These factors must be taken into account in order for LIBS to become a fully quantitative technology that is capable of accurately reporting beryllium concentrations.

## PARTICLES AND STANDARD REFERENCE MATERIALS

The beryllium industry and DOE both advise sampling for airborne beryllium using the inhalable convention instead of closed-face cassette sampling. This is primarily because CBD occurs in the pulmonary region of the lung, and the deposition rate is very poor for particles with aerodynamic diameters greater than 10  $\mu\text{m}$ . Ultrafine particles have also been shown to have a significant role in the development of CBD. Traditionally, technologies such as aerosol cyclones have been used to separate particles of specific size ranges.

Particle morphology also affects how an airborne beryllium sample is collected. Scrap refining and aluminum smelting operations typically generate beryllium oxide fumes in the 0.1–10  $\mu\text{m}$  diameter range. These fumes have a far greater surface area than the large coarse dusts generated in machining operations. Reactivity of the collected sample could be a problem, also. In one case, fine beryllium powders collected at fluoride furnaces and reduction furnaces became solid blocks of material when left undisturbed. Because of the tremendous number of variables involved with beryllium measurement, it is very important to develop and thoroughly characterize a set of standard aerosols that can be used as standard reference materials to characterize and develop emerging technologies, such as LIBS for measuring airborne beryllium.

Beryllium oxide can be prepared at several temperatures. At higher preparation temperatures, more refractory particles are generated, which is increasingly difficult for LIBS to vaporize and measure. LIBS, or any real-time analytical method,

must be able to dissolve even the most refractory materials, such as beryllium oxide prepared at high temperatures. In order to properly develop and characterize a real-time portable instrument designed to detect and measure large airborne particles, large amounts of beryllium oxide and beryllium metal from machining operations must be collected for use as standard reference materials for particles with diameters up to 100  $\mu\text{m}$ . Reference field situations must also be characterized where various species of beryllium may be found.

Ultimately, the performance of real-time portable monitors must be evaluated in various workplace applications to fully validate their usefulness and limitations. Performance-based rather than recipe-based methods are desirable, so investigators can apply them in a wide range of conditions.

## QUALITATIVE VS. QUANTITATIVE

Methods for portable instruments that are not fully quantitative need not be rejected. Much can be learned from qualitative assessments and screening tools. The LIBS technology is one example of this. Indeed, extensive experience with somewhat flawed equipment could give researchers a better idea of how to ultimately develop the best technology that would be both affordable and widely available. 

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The information in this article was based on two presentations that 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) "Methods for Rapid Airborne and Surface Beryllium Measurement Using Portable Technologies: The Current State of the Science" by Kathryn Creek of Los Alamos National Laboratories; and (2) "Performance Testing and Standards for Real-Time Monitoring of Beryllium in Airborne and Surface Contamination" by Mark D. Hoover of the NIOSH Division of Respiratory Disease Studies. The session was arranged by Nicholas J. Lawryk and sponsored by the AIHA Aerosol Technology Committee.

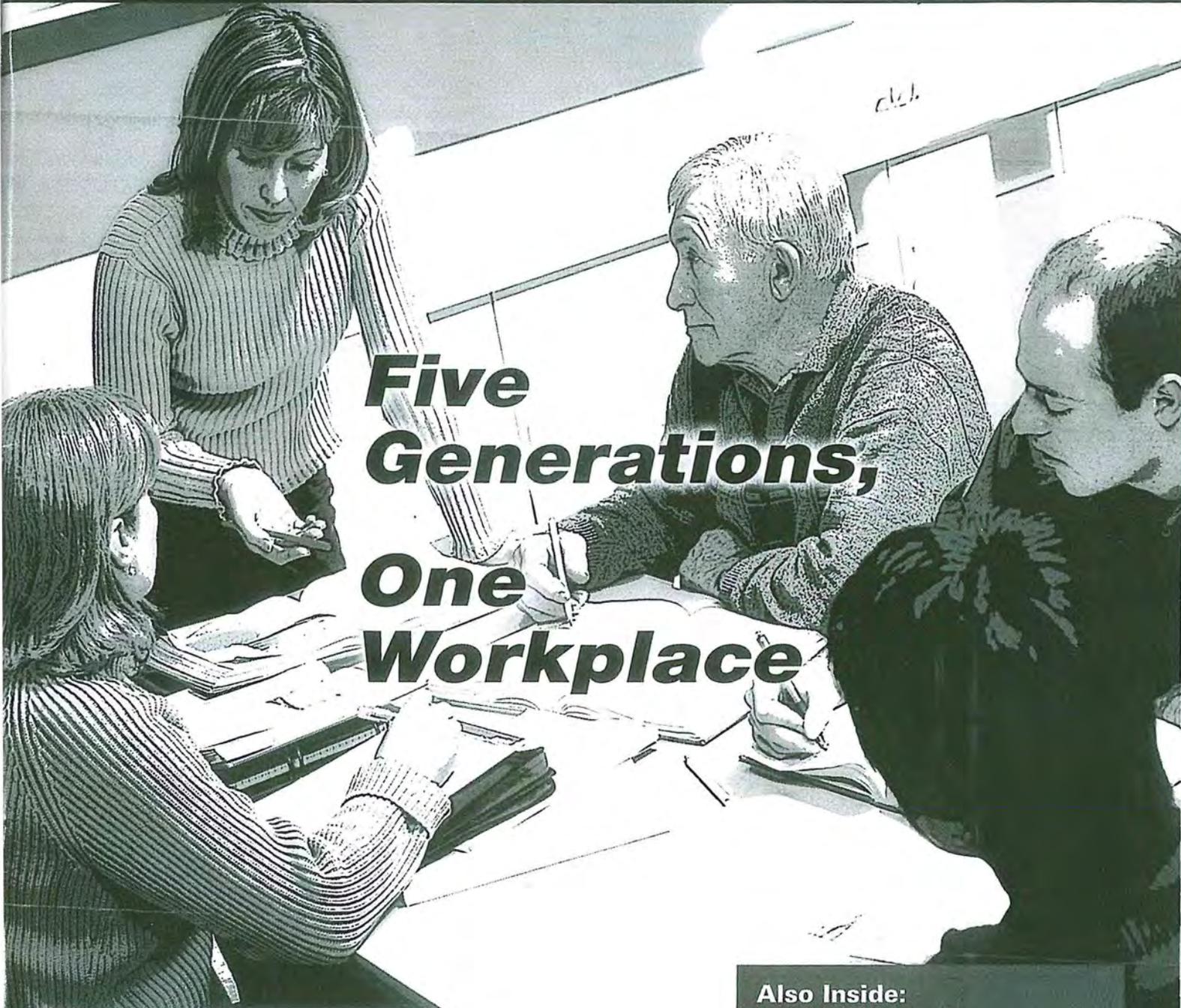


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