



NIOSH HEALTH HAZARD EVALUATION REPORT

**HETA #2003-0328-2935
CPC Pasadena Plastics Complex
Pasadena, Texas**

October 2004



**DEPARTMENT OF HEALTH AND HUMAN SERVICES
Centers for Disease Control and Prevention
National Institute for Occupational Safety and Health**



PREFACE

The Hazard Evaluation and Technical Assistance Branch (HETAB) of the National Institute for Occupational Safety and Health (NIOSH) conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health (OSHA) Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employers or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

HETAB also provides, upon request, technical and consultative assistance to federal, state, and local agencies; labor; industry; and other groups or individuals to control occupational health hazards and to prevent related trauma and disease. Mention of company names or products does not constitute endorsement by NIOSH.

ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Manuel Rodriguez, CIH, CSP, of HETAB, Division of Surveillance, Hazard Evaluations, and Field Studies (DSHEFS). Field assistance was provided by Chandran Achutan, PhD., Ron Sollberger, CHMM, and Trang Nguyen, M.D. Analytical support was provided by DataChem Laboratories. Desktop publishing was performed by Robin Smith and Ellen Blythe. Review and preparation for printing were performed by Penny Arthur.

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Highlights of the NIOSH Health Hazard Evaluation

Evaluation of Employee Exposures to Chromium VI

On July 27, 2003, the National Institute for Occupational Safety and Health (NIOSH) received a confidential request for a Health Hazard Evaluation (HHE) of potential chromium exposure at the Chevron Phillips Chemical Company (CPC) Pasadena Plastics Complex in Pasadena, Texas. The request was submitted by the Paper, Allied-Industrial, Chemical and Energy (PACE) Workers International Union Local 4-227. PACE was concerned about management's policy toward health and safety issues pertaining to chromium catalyst and was interested in information on the short-term and long-term effects associated with exposure to trivalent chromium (CrIII) and hexavalent chromium (CrVI).

What NIOSH Did

- We took air samples to measure employee exposure to CrVI in the activated catalyst.
- We talked to employees about their jobs and health concerns.
- We looked at Chevron Phillips's Chromium Catalyst Health and Hygiene Program.

What NIOSH Found

- Chromium air samples were below the OSHA and NIOSH limits.
- Chevron Phillips Chemical Complex has an adequate control program to protect employees from exposures to chromium.
- Some company health and safety policies are unclear.
- No symptoms or health effects related to chromium exposure were reported to NIOSH investigators.

What Chevron Phillips Chemical Company Managers Can Do

- Review and revise procedures to make sure they are easily understood.
- Continue periodic worker training for occupational exposure to chromium.
- Continue periodic air monitoring and wipe sampling for chromium (VI).

What the Chevron Phillips Chemical Company Employees Can Do

- Report spills right away. Don't try to clean a spill if you are not trained.
- Follow the guidelines in the company Health and Hygiene Program.
- Wear personal protective equipment as required by company procedures.



What To Do For More Information:
We encourage you to read the full report. If you would like a copy, either ask your health and safety representative to make you a copy or call 1-513-841-4252 and ask for HETA Report #HETA 2003-0328-2935



Health Hazard Evaluation Report 2003-0328-2935 CPC Pasadena Plastics Complex Pasadena, Texas October 2004

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SUMMARY

On July 27, 2003 the National Institute for Occupational Safety and Health (NIOSH) received a Health Hazard Evaluation request from the Paper, Allied-Industrial, Chemical and Energy (PACE) Union expressing concerns about employee exposures to hexavalent chromium (CrVI) at the Chevron Phillips Chemical Company (CPC) Pasadena Plastics Complex, Pasadena, Texas. Chromium is used at the facility as a catalyst in the polyethylene production process.

On September 3 and 4, 2003 NIOSH investigators toured the facility, reviewed records, and conducted confidential employee interviews. Due to the limited personal air sampling data available and the potential for employee exposures while replacing components and transferring catalyst, a more in-depth follow-up site visit which included additional confidential employee interviews, air sampling and surface wipe sampling for CrVI was conducted on October 20-24, 2003. Air sampling results were below all applicable occupational exposure limits. Wipe sample results were inconclusive due to the high concentration of CrVI found in the media blanks.

NIOSH investigators concluded that no hazard from exposure to CrVI exists. Personal and area air sampling results for CrVI samples collected during this Health Hazard Evaluation were below applicable occupational exposure limits. Employees reported no symptoms related to chromium exposure. CPC Pasadena Plastics Complex has an adequate program to protect their employees from being overexposed to CrVI. Recommendations for improving the Chromium Catalyst Health and Hygiene Program are provided in this report.

Keywords: SIC 2821 (Plastics Materials, Synthetic Resins, and Nonvulcanizable Elastomers), hexavalent chromium, carcinogen, polyethylene, wipe samples.

Table of Contents

Preface.....	ii
Acknowledgments and Availability of Report.....	ii
Highlights of Health Hazard Evaluation	iii
Summary.....	iv
Introduction.....	1
Background	1
Catalyst Activation.....	1
Polyethylene Production.....	2
Chromium Catalyst Health and Safety	2
Occupational Physicals	2
Personal Protective Equipment	2
Controls.....	3
Training	4
Methods.....	4
Initial site visit	4
Follow-up site visit.....	4
Air Sampling – Total Hexavalent Chromium	4
Air Sampling – Trivalent Chromium.....	5
Ultrafine Particles	5
Wipe Sampling – Total Hexavalent Chromium	5
Employee Interviews.....	5
Evaluation Criteria	6
Chromium.....	6
Chromium (VI).....	7
Chromium (III)	8
Results	8
Observations	8
Initial Site Visit.....	8
Follow-up Site Visit.....	8
Interviews.....	8
OSHA 300 Log.....	9

Industrial Hygiene Sample Results	9
Hexavalent Chromium	9
Hexavalent Chromium Short Term Exposure Monitoring Results	9
Chromium (III)	9
Wipe Samples-Hexavalent Chromium.....	9
Ultrafine Particles	9
Discussion	9
Conclusions.....	10
Recommendations.....	10
References.....	11

INTRODUCTION

On July 27, 2003 the National Institute for Occupational Safety and Health (NIOSH) received a confidential request for a Health Hazard Evaluation (HHE) of potential chromium exposure at the Chevron Phillips Chemical Company (CPC) Pasadena Plastics Complex in Pasadena, Texas. The request was submitted by the Paper, Allied-Industrial, Chemical and Energy (PACE) Workers International Union Local 4-227. PACE was concerned about management's policy toward health and safety issues pertaining to chromium catalyst and was interested in information on the short-term and long-term effects associated with exposure to trivalent chromium (CrIII) and hexavalent chromium (CrVI).

NIOSH investigators conducted an initial site visit on September 3 and 4, 2003. On September 3, 2003 an opening conference held by NIOSH investigators was attended by CPC Pasadena Plastic Complex management, health and safety, and union representatives. Following the meeting, NIOSH investigators toured the facility, conducted confidential employee interviews and reviewed exposure and medical monitoring records. At the closing conference on September 4, 2003 NIOSH investigators discussed preliminary findings. Based on employee concerns, the low occupational exposure limits for CrVI, the limited personal air sampling data, and the potential for exposures to occur when breaking into the closed loop system, the NIOSH investigators determined that a follow-up visit was necessary to better characterize worker exposures to CrVI. During the follow-up visit conducted on October 20-24, 2003 additional employee interviews were conducted, the health and hygiene program was reviewed, tasks with a potential for chromium exposure were observed, and personal air samples and wipe samples for CrVI were collected. During the closing conference for this visit NIOSH investigators again presented preliminary findings and recommendations.

BACKGROUND

The CPC Pasadena Plastics Complex facility produces 2.2 billion pounds of polyethylene, 810 million pounds of polypropylene, and 310 million pounds of K-Resin per year. The Pasadena Plastics Complex sits on approximately 650 acres and has been in operation since 1949. The first high density particle form polyethylene plant was built in 1961; polypropylene production began in 1971 and K-resin production began in 1979. In 1982 a small organic liquids plant was built for specialty chemicals. Between 1990 and 1992 polyethylene plants VI, VII, and VIII were built.¹ Although 750 employees are assigned to the CPC Pasadena Plastics Complex the 150 operations and maintenance personnel working at plants VI, VII, and VIII where chromium catalyst is handled were the focus of this evaluation.

Polyethylene is produced at the CPC Pasadena Plastics Complex by the polymerization of ethylene in tubular reactors. The polymerization process for high-density polyethylene relies on a catalyst to create an active site for polymerization. CrIII bound to silica is heated and the CrIII is reduced to CrVI. This product is called activated catalyst and is used to produce high-density polyethylene. Polymerization is achieved by the reaction of the catalyst with an olefin. The olefin reduces the valence state of the transition metal atoms, thus making it more reactive. For the catalyst to be effective it must be in the hexavalent state.

Catalyst Activation

The raw catalyst (unactivated) is in a trivalent chromium state and consists primarily of 80-99% silicon dioxide and 0.1-3% chromium acetate. The catalyst is manufactured by fixing CrIII compounds to amorphous silica. The raw catalyst is not capable of producing the proper polymer until it is activated for use. The activation process heats the catalyst to 1600°F in a Catalyst Activator, removing moisture and changing the valence of the chromium from +3 to a +6 charge.² The catalyst arrives in metal or

fiber drums which are stored in the catalyst warehouse. When the catalyst is needed for activation it is moved to the activator bay by forklift. A high pressure hose is connected to the drums to transfer the catalyst to a weigh bin located on the top of the activator. The weigh bin weighs the catalyst to ensure the correct amount of catalyst will be charged to the activator as required by the recipe. After the catalyst has been weighed and the activator is ready, the catalyst is charged (transferred) to the activator. The activator acts like a furnace, heating and holding (8-15 hours depending on the catalyst) the catalyst at a desired temperature until the catalyst has been activated. The catalyst is allowed to cool and then purged with nitrogen before being dumped into a metal tote bin. Once in the tote bin, the catalyst is again purged with nitrogen to remove any remaining oxygen and is ready for use by the reactors in any of the three polyethylene plants.

Polyethylene Production

The activated catalyst is transported to the reactor area in tote bins under nitrogen pressure to prevent contamination by air which could reduce the catalyst and make it unusable for polymerization. In a process called charging the catalyst is transferred from the tote bins to the mud pots on the sixth level of the reactor. In the mud pots the granular catalyst is mixed with an olefin-free isobutane creating slurry (mud) in the mud pot. Ball-check feeders meter the amounts of catalyst mud dumped into the reactors. The catalyst reacts with the ethylene in the reactors to form powdered polyethylene (fluff) which is then transferred to silos. From the silos the fluff is heated, extruded, and mixed with additives then transferred to a pelletizer by pneumatic pressure. The pellets are loaded on hopper carts and transferred to the customer.³

Chromium Catalyst Health and Safety

The entire activation and reaction process is closed loop. The highest potential for personnel to be exposed to the activated chromium catalyst is while connecting and disconnecting transfer lines, collecting activated catalyst samples for

laboratory analysis, or in the event of a spill. Chevron Phillips treats CrVI as a human carcinogen and has implemented a health and hygiene program to control exposure to chromium catalyst. The program provides for the use of personal protective equipment (PPE), decontamination facilities, waste disposal, wipe testing, contract laundering of contaminated clothing, training, and medical monitoring. The program also has guidelines for the supervision of contractors working in areas where catalyst is handled and provides for all contractors to receive a copy of the Chromium Catalyst Health and Hygiene Program and Material Safety Data Sheets for the catalysts.⁴

Occupational Physicals

Annual medical surveillance exams specific for chromium are provided to operations personnel assigned to the catalyst activation unit. Employees are also provided a termination exam specific for potential chromium health effects if they will no longer be working at the Activation Unit due to retirement or reassignment. A chrome catalyst examination includes the following: complete blood count, chemistry profile, urinalysis, spirometry, resting electrocardiogram (every five years at age 45), chest x-ray (initial then every five years unless clinically indicated), urine chromium, completion of a medical exam form, and the examining physician's written opinion.

Personal Protective Equipment

Chevron Phillips has characterized work activities as Categories A, B, and C based on a qualitative assessment of the potential for employees to come in contact with the chromium catalyst. Category A designates activities where it is anticipated no exposure to chromium catalyst will occur and includes touring facilities or inspecting catalyst containing equipment without opening it, and maintenance activities involving non-catalyst containing equipment. Category A activities require no special PPE aside from what is normally worn by all plant personnel: Nomex® (flame retardant) coveralls, hard hats, safety

glasses or goggles, hearing protection and safety shoes. Category B is for activities with a “slight” potential for chromium exposure. These are activities where the catalyst should remain in the process piping, but there is a slight chance for it to be present in some fittings. Examples of this type of activity are inspection of open catalyst containing equipment, opening of purged transfer hoses, and other activities that may involve catalyst emissions. Category B activities require the use of Pyrolon® (chemical resistant, fire retardant) coveralls over Nomex® coveralls, gloves, and half-face or full-face air purifying respirators with High Efficiency Particulate Air (HEPA) filters. Category C is for work activities with a “moderate” potential for exposure to chromium catalyst. Category C activities are those in which there is a potential that the employee will come into contact with the catalyst. Category C activities will require that decontamination procedures be followed. Category C activities require the use of Pyrolon® disposable coveralls, temporary Nomex® cloth coveralls, impervious gloves, a half-face or full-face air purifying respirator with HEPA filters, goggles, socks, rubber boots and overshoes.

All air purifying respirators worn by personnel at the Chevron facility are manufactured by 3M. CPC has a variety of gloves available for personnel to use according to the potential exposure. For chemical protection the following gloves are available: butyl rubber, ethylene vinyl alcohol, nitrile, neoprene, and polyvinyl chloride. The *Quick Selection Guide to Chemical Protective Clothing* recommends butyl rubber, nitrile, or polyvinylchloride for protection against chromic acid.⁵ Special gloves are available for welding, electrical work, medical, and laboratory. Cut resistant gloves are also available. For tasks where exposure to catalyst may occur, orange Nomex® coveralls are used under the Pyrolon® coveralls. Orange Nomex® are placed in a container for contaminated clothing after use so they can be cleaned by contract laundering. Blue Nomex® may be contaminated with chromium catalyst during certain activities. Employees have been instructed that if they believe the coveralls are

contaminated they should place them in the contaminated clothing container for contract laundering; otherwise employees take coveralls home for laundering.

Controls

Chevron Phillips has implemented various controls to limit exposures to chromium catalyst. Employees desiring access to the Catalyst Activators or the Reactor Plants must sign in at the Control Room for each facility. Warning signs have been posted identifying chromium hazards areas. As a control measure, work activities are characterized to identify tasks with a potential for exposure to chromium catalyst. When Category B or C activities are performed the area is controlled through the use of barrier tape. Polyethylene sheets are placed under the components to catch any catalyst that may fall when replacing or removing components from a system that contains catalyst. When a component is removed, the component and the site where it was installed are cleaned with a HEPA vacuum. When a component is to be removed both the operator and the maintenance specialist must verify which component requires removal by touching the component. Lock out and tag out (LOTO) is accomplished before a component containing catalyst is removed. LOTO must be verified by the operator and the maintenance specialist. Lines used to transfer catalyst are purged prior to disconnecting. Personnel performing Category B and C activities must follow established decontamination procedures after completing the task. Chevron Phillips has decontamination facilities with a dirty room, showers, and a clean room. Lockers are available in the clean room. Contaminated articles are placed in special containers and labeled for disposal. The Chemical Complex operates under the Occupational Safety and Health Administration (OSHA) standard 29 CFR 1910.119 Process Safety Management of Highly Hazardous Chemicals.⁶ Any time a process is changed it is reviewed and a process hazard analysis is completed.

Training

CPC has a written Health and Hygiene Program for chromium catalyst dated June 1995. The procedure addresses health hazards associated with chromium, medical surveillance, work activity characterization, PPE, decontamination, waste disposal, spill clean-up, wipe testing, laboratory analysis, warehouse handling of raw catalyst, and procedures to ensure contractors and vendors are not exposed to chromium catalyst. CPC employees at the Pasadena Plastics complex are trained and tested on the contents of the procedure. Training modules have been written to assist employees in performing tasks. The training modules also contain warnings to alert employees of safety and health hazards. The training modules are computer based. A test is given at the end of each module and the employees must pass the test within two tries or they will require special training.

METHODS

Initial site visit

During the tour of the facility, NIOSH personnel visited the catalysts activators, the plant VI reactors and control room, the maintenance facilities, the break rooms, and the decontamination facilities. During the tour, operators in the Plant VI control room were interviewed. On the second day of the visit, personnel were randomly selected from a personnel roster for confidential interviews. Twenty-two of the 150 maintenance and operations employees were interviewed. Employees were queried about their potential exposure to chromium, use of PPE, catalyst spills, surface contamination, and symptoms related to chromium exposure. Occupational safety and health personnel and Union representatives were also interviewed. NIOSH personnel also reviewed the Log of Work-Related Injuries and Illnesses (OSHA Form 300), previous CrVI air sampling data collected by the company, medical records, and chromium catalyst-related incident reports. At the closing conference held September 4, 2003 NIOSH

investigators reported findings of the initial site visit and discussed the possibility of a follow-up visit.

Follow-up site visit

NIOSH investigators conducted a follow-up visit to the CPC Pasadena Plastics Complex October 20-24, 2003. During the follow-up visit NIOSH personnel reviewed the chromium catalyst health and hygiene program, training records, use of PPE, and work controls. Personal air monitoring for CrVI was conducted during day and night shift for operations personnel. Two maintenance personnel were sampled for CrVI. Polyethylene Plant VIII was not in operation at the time of this evaluation.

Air Sampling – Total Hexavalent Chromium

Personal and area air samples for CrVI were collected per NIOSH method 7605 (draft).⁷ Samples were collected using calibrated SKC Air Check-2000 air sampling pumps set to a flow rate of two liters per minute (lpm). Each sampling train consisted of the pump, Tygon® tubing connected to the inlet port of the pump and a 37 millimeter (mm) diameter 5.0 micrometer (µm) pore size polyvinyl chloride (PVC) membrane filter and cassette attached to the end of the Tygon® tubing. The cassette was attached within the employee's breathing zone (breathing zone is defined as an area in front of the shoulders with a radius of 6 to 9 inches) to their lapel or protective suit. All pumps were pre- and post-calibrated. The samples were analyzed for total CrVI by high performance liquid chromatography with post column derivatization and ultraviolet (UV) detection.⁷ No distinction was made as to the solubility of CrVI in the samples.

As of September 2003 there were 91 operators and 65 maintenance employees assigned to work at Plants VI, VII, and VIII, and the catalyst activators. Plant VIII was not in operation at the time of this evaluation due to periodic maintenance. Operations personnel at the plant work 12-hour shifts and maintenance personnel work 8-hour shifts. Personal air monitoring for

CrVI was conducted on all operators on duty during the evaluation. Maintenance personnel were sampled if they were performing activities where they could be exposed to activated catalyst. A total of 43 personal breathing zone samples and three area samples were collected during the evaluation. For personal breathing zone samples the cassette was attached to the employee's collar. Long-term sampling (full-shift) was conducted on 32 operations personnel and two maintenance personnel. Short-term exposure monitoring (<30 minutes) was conducted on five employees performing tasks with a potential for CrVI exposure such as transferring catalyst. Three operations personnel were sampled less than 10 hours due to work schedules, one was sampled less than 10 hours due to a pump failure. A laboratory technician was sampled for one 8-hour shift and one short-term sample was collected while he analyzed samples.

Air Sampling – Trivalent Chromium

One short-term exposure sample for CrIII was collected while an employee charged raw catalyst to a weigh bin. The sample was collected using the same media, flow rate, and procedures used to collect the CrVI samples. The sample was analyzed per NIOSH method 7300 using inductively coupled argon plasma, atomic emission spectroscopy.⁸

Ultrafine Particles

A TSI P-Trak Ultrafine Particle Counter was used to check at the Activators for catalyst leaks. The particle counter does not measure chromium concentration; it is designed to count particles that are less than 0.1 µm in diameter. The P-Trak was used to detect leaks from the Activators, not to determine ultrafine particle concentrations. A rise in the particle count would indicate a potential leak.

Wipe Sampling – Total Hexavalent Chromium

Wipe samples for CrVI were collected by placing a 10 centimeter (cm) by 10 cm plastic template over the surface to be sampled and wiping the exposed surface area with a binderless quartz fiber filter per OSHA method W4001.⁹ The surface area was wiped using an overlapping "S" pattern while applying firm pressure on the filter with the fingertips. Results were reported as micrograms (µg)/100 cm². Where a flat surface was not available, such as fittings for connecting hoses, the object was wiped with the filter without considering the total surface area. Those results are expressed in µg per sample. A clean pair of nitrile gloves was donned to collect each sample. The filter was subsequently placed in a 20 milliliter (ml) glass scintillation vial. Each vial was labeled with a sample identification number. A separate vial was used for each sample. SKC 37 mm diameter, 0.4 mm thick binderless quartz fiber filters (catalogue number 225-1822) were used as recommended by the OSHA method for rough surfaces because they are more durable. The samples were submitted to the DataChem Laboratory for analysis and were analyzed per NIOSH method 7605 using ion chromatography with post-column derivatization and UV detection. Samples submitted for CrVI analysis were analyzed for total CrVI. No distinction was made as to the solubility of CrVI in the samples. Twenty two wipe samples were collected at various locations throughout the polyethylene production area.

Employee Interviews

NIOSH investigators conducted formal, confidential interviews with 22 employees. Thirteen of these workers were the same catalyst and activator operators who participated in the environmental monitoring. The remaining 9 were general and pump and turbine mechanics. Employees were asked their name and age, job title, level of training received with respect to hazards associated with CrVI, concerns regarding health and the work environment, and smoking status.

EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employs environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. However it is important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs),¹⁰ (2) the American Conference of Governmental Industrial Hygienists' (ACGIH®) Threshold Limit Values (TLVs®),¹¹ and (3) the U.S. Department of Labor, (OSHA) Permissible Exposure Limits (PELs).¹² Employers are encouraged to follow the OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever are the more protective criterion.

OSHA requires an employer to furnish employees a place of employment that is free from recognized hazards that are causing or are likely to cause death or serious physical harm

[Occupational Safety and Health Act of 1970, Public Law 91-596, sec. 5(a)(1)]. Thus, employers should understand that not all hazardous chemicals have specific OSHA exposure limits such as PELs and short-term exposure limits (STELs). An employer is still required by OSHA to protect their employees from hazards, even in the absence of a specific OSHA PEL.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8- to 10-hour workday. Some substances have recommended STEL or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short-term.

NIOSH and OSHA have published validated analytical methods for sampling and analysis of many hazardous chemicals. NIOSH field staff employ these methods for personal exposure and area air monitoring. Air samples are collected using the prescribed media and sampling rate and submitted for analysis to an AIHA accredited laboratory. Pumps used for air sampling are pre and post calibrated using a NIST traceable primary calibration standard. For personal air samples the collection media is placed in the employees breathing zone (normally within six inches of the nose). Air sampling results are compared to NIOSH RELs, OSHA PELs, or ACGIH TLVs.

Chromium

Chromium is a naturally occurring element found in rocks, animals, plants, soil and in volcanic dust and gasses. Chromium is present in the environment in several different forms. The most common forms are chromium (0), CrIII, and CrVI.¹³ In humans and animals, CrIII is an essential nutrient that plays a role in glucose, fat, and protein metabolism by potentiating the action of insulin in body tissues. The U.S. Natural Research Council has recommended a daily chromium intake of 50 to 200 milligrams (mg).¹⁴ Chromium (0) and CrVI are generally produced by industrial processes. Chromium enters the air, water, and soil mostly

in the CrIII and CrVI forms as a result of both natural processes and human activities.¹³ Chromium is found in many foods such as fruits, vegetables, dairy products, meat, seafood, and canned foods in concentrations of 20-500 micrograms per kilogram ($\mu\text{g}/\text{kg}$).¹⁵ The general population is exposed to chromium by inhaling ambient air, ingesting food, and drinking water containing chromium.¹⁵ Chromium may enter the human body through three different routes: through the airways, through the gastrointestinal tract, and through the skin, specially injured skin.¹⁴ Occupational exposures to chromium occur mainly from chromate production, stainless steel production and welding, chrome plating, and tanning; however there are many other occupations in which workers are exposed to chromium. People may be exposed to higher levels of chromium if they use tobacco products (since tobacco contains chromium) or by consuming supplements containing chromium.¹³ Studies have revealed an increase in urinary total chromium among smoking welders as compared with nonsmoking welders.¹⁴ Under normal conditions, CrIII and Chromium(0) in the air undergo no reaction in the environment. CrVI in the air eventually reacts with dust particles to form CrIII; however the exact nature of such atmospheric reactions has not been studied extensively. Chromium is removed from air by atmospheric fallout and precipitation. How quickly this occurs depends on the particle size and density.¹⁶ Chromium has no odor or warning properties.

Chromium (VI)

NIOSH considers CrVI to be a potential occupational carcinogen based upon research suggesting a relationship between CrVI exposures and the development of lung cancer. CrVI is classified as a human carcinogen by ACGIH, the Environmental Protection Agency (EPA), and the World Health Organization.¹⁷ The toxicity and solubility of compounds that contain chromium in the CrII, CrIII, or CrVI valence states vary greatly; those that contain CrVI cause the greatest health concern. CrVI compounds include lead chromate and zinc chromate pigments, chromic acid, and soluble compounds such as those used in chromium

plating. Some CrVI compounds are severe irritants of the respiratory tract and skin, and some (including chromates) have been found to cause lung cancer in exposed workers. CrVI is corrosive and causes chronic ulceration and perforation of the nasal septum.¹⁸ It also causes chronic ulceration of other skin surfaces. Allergic dermatitis is one of the most common effects of chromium toxicity among exposed workers. CrVI compounds are taken up through the skin to a limited extent, while CrIII compounds penetrate with great difficulty. CrVI readily penetrates cell membranes and once inside the cell it is reduced to CrIII. Once inside a cell CrIII has the capacity to cause DNA damage. The NIOSH REL for a 10-hour TWA exposure to airborne CrVI is 1.0 micrograms per cubic meter ($\mu\text{g}/\text{m}^3$). NIOSH has set an immediately dangerous to life and health (IDLH) limit for CrVI of 15 milligrams per cubic meter (mg/m^3). The applicable OSHA PEL for CrVI trioxide (chromic acid, or CrO_3) is a "ceiling" of 100 μg (CrO_3)/ m^3 this is equivalent to 52 μg (CrVI)/ m^3 . CrVI compounds tend to be of low solubility in water and thus are subdivided into two subgroups by ACGIH, water soluble and water-insoluble. The ACGIH TLVs are 50 $\mu\text{g}/\text{m}^3$ for water-soluble CrVI compounds and chromates, and 10 $\mu\text{g}/\text{m}^3$ for insoluble CrVI compounds; these exposure criteria apply to full-shift TWA exposures of 8 hours. Biological monitoring for chromium has not been found useful in assessing chromium exposure because CrVI is reduced to CrIII in the body and CrIII is ubiquitous. It is found in water, air, food, tobacco, and dietary supplements.¹⁹ Levels of chromium compounds in humans have to be relatively high before they signify an increase due to exposure. Since CrVI is reduced to CrIII in red blood cells, the level of chromium in red blood cells is an indication of CrVI exposure. Since red blood cells last up to 120 days, the presence of chromium in red blood cells can indicate if a person was exposed from one to 120 days prior to the test. Analysis of biological samples is further complicated by the lack of Standard Reference Materials.¹³

Chromium (III)

CrIII as stated above occurs naturally in the environment and is an essential nutrient. OSHA has set an 8-hour PEL-TWA of 0.5 mg/m³ for CrIII. The ACGIH has recommended an 8-hour TLV-TWA of 0.5 mg/m³ for chromium metal and trivalent chromium compounds to minimize the potential for respiratory tract and dermal irritation and dermatitis. This TLV was adopted in 1931 for chromium metal dust.¹¹ Since that time ACGIH has not become aware of any reports of adverse health effects from CrIII so the TLV has been retained. ACGIH has classified CrIII as not a human carcinogen. The NIOSH Recommended Exposure Limit for a 10-hour TWA exposure to CrIII is 0.5 mg/m³. NIOSH has set an IDLH limit for soluble trivalent chromium salts of 250 mg/m³.

RESULTS

Observations

Initial Site Visit

While touring the Catalyst Activators NIOSH investigators noted catalyst on top of a tote bin. Safety personnel indicated this was very unusual, some employees indicated it was a common occurrence.

Follow-up Site Visit

NIOSH investigators observed employees transferring activated catalyst while charging the mud pots and transferring raw catalyst to the activator. No visible emissions of catalyst were noted during the transfer processes. During the three days NIOSH investigators were sampling, only two maintenance personnel performed tasks with a potential for exposure to chromium catalyst. Between January 1, 2003 and October 14, 2003 approximately 120 Category C activities were performed at the catalyst activators. That equates to approximately 13 Category C activities per month.

Interviews

Catalyst operators reported that pre-placement physical exams are done initially and that respiratory fit testing and pulmonary function tests are done annually. Interviewed employees reported that the specific PPE requirements for handling spills (whether to wear level B or level C suits) depend on the catalyst operator's judgment. Use of the decontamination room is based on the judgment of the operator. Catalyst operators' responses concerning the handling of spills of chromium were inconsistent. Some operators reported, "We vacuum the spills," while others replied, "we wet it down," and still others responded, "we notify the supervisor if the spill is large." Additionally, catalyst operators reported contractors working in activated chromium areas were often seen with inappropriate protective work clothing and respirators.

The catalyst and activator operators were generally satisfied with the training received. All of them knew cognizant that CrVI is a human carcinogen. They also felt that they were provided with adequate PPE to perform their job, and said that they were all part of a medical surveillance program for chromium. None reported any health problems thought to be work related. The operators ranged in age from 36 to 57 years, and have spent between 7 and 23 years on the job.

Due to the mobility associated with their job, mechanics were interviewed during breaks at their break room. Most of the mechanics said that CrVI is an animal carcinogen or a suspected human carcinogen. The mechanics are part of a respiratory and hearing conservation program, but not a medical surveillance program for chromium. Mechanics voiced concern about walking through dusty areas of the workplace without PPE. Some of the employees acknowledged that they don their respirators when not clean shaven. Mechanics are exposed to CrVI when opening up lines and vessels, and when working on catalyst feeders. The mechanics ranged in age from 43 to 56 years, and have spent between 10 and 27 years on the job.

OSHA 300 Log

The OSHA 300 Form, Log of Work Related Injuries and Illnesses for years 2002 and 2003 revealed five work related injuries with days away from work in 2002. As of September 2003 there were two recorded cases with workdays lost for 2003. None of the recorded injuries or illnesses for 2002 and 2003 involved chromium catalyst exposure.

Industrial Hygiene Sample Results

Hexavalent Chromium

Personal full-shift air monitoring results for CrVI are shown in Table 1. Sample results ranged from 0.06 to 0.49 $\mu\text{g}/\text{m}^3$. Once personal samples were blank corrected most of the results were below the minimum detectable concentration. Without blank correcting, sample concentrations were below all of the relevant evaluation criteria.

Hexavalent Chromium Short-Term Exposure Monitoring Results

Personal short-term exposure monitoring results for CrVI are shown in Table 2. Sample results ranged from 2.29 to 3.60 $\mu\text{g}/\text{m}^3$ without field blank correction. After blank correction most of the sample results were below the minimum detectable concentration. Even without blank correction the sample results are still much lower than the OSHA evaluation criteria of 100 $\mu\text{g}/\text{m}^3$ as CrO₃ or 52 $\mu\text{g}/\text{m}^3$ CrVI mentioned on p. 7.

Chromium (III)

A short-term exposure monitoring sample was collected while transferring raw catalyst to the weigh bin at the Catalyst Activator. A concentration of 2 μg was detected in the sample. The total volume of air collected was 60 liters or 0.060 m^3 . The TWA for the sample period was 33 $\mu\text{g}/\text{m}^3$. There is no short-term exposure limit or ceiling limit for CrIII. However the results are below the OSHA PEL,

the ACGIH 8-hour TLV-TWA, and the NIOSH REL, indicating that this task did not constitute an excursion above the applicable occupational exposure limits.

Wipe Samples-Hexavalent Chromium

Laboratory analysis of media blanks indicated that the binderless quartz fiber filters used to collect the wipe samples contained levels of CrVI above the limit of quantification (LOQ) and above the OSHA target concentration of 0.05 $\mu\text{g}/100 \text{ cm}^2$. The filters used are the appropriate media recommended by OSHA method W4001. Given the high concentration of chromium detected in the media blanks the sample results cannot be used to derive any conclusions about the levels of surface contamination in the sampled areas.

Ultrafine Particles

A TSI P-Trak Ultrafine Particle Counter was used to check the Activators for catalyst leaks. No leaks were detected while walking up and down the structures and no visible emissions were seen. The particle counts in particles per cubic centimeter (p/cc) outside plants VI and VII were around 40,000 p/cc. Inside the control rooms for each respective plant, the particle count was around 1000 p/cc indicating that outside air is not entering the control rooms.

DISCUSSION

The basis of the HHE request was concern about CPC Pasadena Plastics Complex management's policy on the health hazards of chromium. Although CrVI is classified as a potential human carcinogen by NIOSH, EPA, ACGIH, and other organizations, the HHE requestor was concerned that the company considers CrVI a suspect human carcinogen. CPC management reported to us that CPC has considered CrVI a suspected human carcinogen because a report by the IARC states, "There is limited evidence in experimental animals for the carcinogenicity of chromium trioxide (chromic acid) and sodium dichromate." However, IARC has given CrVI an

overall classification of Group I, carcinogenic to humans, and NIOSH considers CrVI to be a potential human carcinogen.

As used at the CPC polyethylene production process, CrVI is bound to amorphous silica. This raises questions as to the bioavailability of the CrVI once it enters the body. The health effects of CrVI are based on the reduction of CrVI to CrIII after the CrVI crosses a cell membrane. It is possible that if CrVI remains bound to the silica particle, it may not be able to cross the cell membrane, and therefore not have the same toxicity as unbound CrVI. However, no studies have been conducted to prove or disprove this theory, and we are unable to comment on the possible altered toxicity of bound CrVI.

Another concern raised in the HHE request was related to the potential for health effects related to past exposure to CrVI. We cannot comment on CPC Pasadena Plastics Complex worker exposure to CrVI during times for which there are no industrial hygiene sampling data.

A final concern mentioned in the HHE request was that employees have been told CrVI reverts to CrIII when it contacts the air. In the Tenth Report on Carcinogens, IARC states that hexavalent compounds are generally reduced to the trivalent state in the environment. However this does not mean that all the CrVI released will be immediately reduced. CrVI is a health hazard when released and may remain a health hazard for a week or longer. The estimated half-life for CrVI reduction to CrIII in air was reported in the range of 16 hours to 5 days.²⁰

CONCLUSIONS

The following conclusions were drawn from our work in this HHE:

1. CPC appears to have a comprehensive health and safety program in place at the Pasadena facility with regard to potential occupational exposure to chromium. Based on the findings of this evaluation, NIOSH investigators concluded that the controls CPC has implemented at the Pasadena Plastics

Complex are adequate to prevent employees from being exposed to CrVI above applicable exposure limits.

2. Personal air sampling results for CrVI indicate that none of the CPC Pasadena Plastics Complex employees sampled were exposed to CrVI above relevant exposure criteria, including the NIOSH 10-hour REL-TWA and the OSHA Ceiling limit, during this evaluation.

3. No conclusions can be provided about our evaluation of potential surface contamination because the concentrations of CrVI detected in the sampling media blanks by the laboratory were above the limit of quantitation and above the OSHA target concentration of 0.050 µg/100 cm². However, during our walkthrough, uncontained catalyst was seen on top of a tote bin, in fittings, in a bucket, and on the table where the sample flasks are stored. This suggests that there is a need to address housekeeping and catalyst handling procedures.

4. None of the employees interviewed reported symptoms that could be associated with chromium exposure.

RECOMMENDATIONS

The CPC Pasadena Plastics Complex health and hygiene program for occupational exposure to chromium appears effective in minimizing occupational exposure to chromium among workers and should be continued. The following recommendations may help improve the program.

1. Provide specific guidance regarding when coveralls are considered contaminated rather than leaving this to employee judgment. Employees have indicated some confusion regarding when the company should launder contaminated or potentially contaminated coveralls and when they should launder their coveralls at home. Clothing used in a chromium regulated area should be considered contaminated.

2. Educate workers in the polyethylene production areas and other workers potentially

exposed to chromium concerning the aspects of the CPC Pasadena Plastics Complex health and hygiene program that address occupational exposure to chromium.

3. Modify the activated chromium catalyst sampling process to avoid release, spills, or flask contamination. A possible solution is using vacuum cylinders to collect samples or some type of engineering control such as a glove box to prevent the release of catalyst when it is transferred to the flask. The sample flask may be wiped in the glove box before it is removed.

4. Maintain all work areas free of chromium catalyst, especially the tool room where sampling flasks are stored.

5. Avoid using water hoses to perform various activities in the production area because the water pressure can cause catalyst to become airborne. The recommendation is based on an incident report that indicates that an employee was sprayed with catalyst while checking the consistency of material in a quench drum with a water hose. In another incident a water hose was used to wash spilled catalyst into a trench.

6. Collect dry catalyst with a HEPA vacuum. Use shoveling, dry sweeping, and dry clean-up of chromium only where neither vacuuming nor wet cleaning are feasible.

7. Train catalyst operators and maintenance personnel periodically concerning proper response methods for spills or leakage and concerning appropriate PPE use.

- a) Standardize PPE requirements and decontamination procedures.
- b) Spills and leaks should only be cleaned by properly trained personnel.
- c) Investigate the cause of incidents in which catalyst is found on a work surface or in some other uncontrolled form where employees could be exposed.
- d) All aspects of the chromium catalyst health and hygiene program should also apply to contractors who work with activated chromium.

8. Store catalyst in sealed containers rather than open buckets. If workers use a bucket to collect catalyst, the catalyst should be promptly transferred to a sealed container or properly disposed.

9. Affix warning labels to all materials, mixtures, scrap, waste, debris, equipment, and other products containing chromium. Bag and tag contaminated tools if they are not immediately cleaned.

10. Review training modules to ensure that language and instructions clearly and explicitly describe requirements. For example, p.6 of Module 05.01 lists precautions as follows:

- a) Wear additional PPE:
 - Respirator and filter – (*What type, what filters?*)
 - Rubber gloves – (*What type?*)

b) Launder contaminated clothing before reuse. (*Does this mean employees should wash the coveralls or should they place the coveralls in the container for contaminated clothing to be washed by contract services?*)

c) Shower if necessary. (*The nature of the task and the potential exposure should dictate when employees shower. Avoid leaving this to employees to decide.*)

11. Ensure that employees have shaved properly prior to donning respirators. Mechanics commented that this may require closer supervision.

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Table 1
Hexavalent Chromium Full-Shift Personal Samples
HETA 2003-0328-2935
CPC Pasadena Plastics Complex
Pasadena, Texas
October 20-24, 2003

Date Collected	Sample#	Job Title	Lab Result (µg/sample)*	Sample Volume (Liters)	10-hour TWA (µg/m ³)**
10/20/03	BZP6-01	Chief Operator Plant VII	0.16	1347	ND
10/20/03	BZP6-02	Chief Operator Plant VI	0.13	1268	ND
10/20/03	BZP6-03	#1 Operator Plant VI	0.22	1230	Trace
10/20/03	BZP6-04	Activator Operator Plant VI	0.21	474#	N/A
10/20/03	BZP6-05	Chief Operator Plant VI	0.17	1214	Trace
10/20/03	BZP7-01	Chief Operator Plant VII	0.10	1337	ND
10/20/03	BZP7-02	#1 Operator Plant VII	0.13	1325	ND
10/21/03	BZP8-01	Activator Operator Plant 6	0.24	1218	0.09
10/21/03	BZP8-02	Activator Operator Plant 6	0.24	1222	0.09
10/21/03	BZP8-03	Chief Operator Plant 6	0.11	1207	ND
10/21/03	BZP8-04	Chief Operator Plant 6	0.12	1206	ND
10/21/03	BZP8-05	Reactor #1 Operator Plant 7	0.24	1215	0.09
10/21/03	BZP6-08	Activator Operator Plant 6	0.27	1162	0.12
10/21/03	BZP6-09	Activator Operator Plant 6	0.12	1197	ND
10/21/03	BZP6-10	Reactor #1 Operator Plant 6	0.17	1209	Trace
10/21/03	BZP7-03	Activator Operator Plant 7	0.22	1178	Trace
10/21/03	BZP7-04	Chief Reactor Operator Plant 7	0.10	1166	ND
10/21/03	A-01	Activator area sample	0.07	1122	ND
10/21/03	A-02	Activator area sample	0.08	1121	ND
10/21/03	A-03	Men's Decon trailer clean room	0.17	985	Trace
10/21/03	BZL-01	Laboratory Technician	0.17	893	Trace
10/21/03	BZP6-11	Plant 6 Reactor #1 Operator	0.10	538	ND

An average blank concentration of 0.13 µg/sample was subtracted from the sample results before calculating the 10-hr TWA. Where the 10-hour TWA was <0.03 µg/m³ the results were reported as ND (non-detected). Results between 0.03 µg/m³ and 0.08µg/m³ were reported as Trace.

* This is the total amount of hexavalent chromium collected on the sample media during the sample period.

** The 10-hour TWA was calculated by dividing the sample volume (amount of air) by 1000 to convert to cubic meters, then dividing the lab result by the # of cubic meters. The resulting air concentration was multiplied by the sampled time and then divided by 600 minutes. **The NIOSH 10-hour REL-TWA, Recommended Exposure Limit is 1µg/m³.** Any result listed in this column that is over 1.00µg/m³ will be considered as being over our limit.

Pump faulted.

LOD = 0.04 µg/sample. LOD is the lowest concentration that can be detected above background noise and that is specific to the analytical procedure used.

LOQ = 0.10 µg/sample. LOQ is the lowest concentration that can be quantified with confidence and that is specific to the analytical procedure used

MDC= 0.03 µg/m³. MDC is the minimum detectable concentration for a given a sample volume. The MDC was calculated by dividing the LOD by 1.2 m³.

MQC= 0.08µg/m³. MQC is the minimum quantifiable concentration for a given sample volume. The MQC was calculated by dividing the LOQ by 1.2 m³.

Table 1 (continued)
Hexavalent Chromium Full-Shift Personal Samples
HETA 2003-0328-2935
CPC Pasadena Plastics Complex
Pasadena, Texas
October 20-24, 2003

Date Collected	Sample#	Job Title	Lab Result (µg/sample)*	Sample Volume (Liters)	10-hour TWA (µg/m ³)*
10/22/03	BZP6-1	Activator Operator Plant 6	0.64	1299	0.39
10/22/03	BZP6-3	Activator Operator Plant 6	0.13	1208	nd
10/22/03	BZP6-4	Plant 6 Reactor #1 Operator	0.24	1208	0.09
10/22/03	BZP6-5	Plant 6 Reactor #1 Operator	0.17	1206	Trace
10/22/03	BZP6-6	Chief Operator Plant 6	0.22	1209	Trace
10/22/03	BZP7-01	Chief Operator Plant 7	0.08	1025	ND
10/22/03	BZP7-02	Chief Operator Plant 7	0.13	913	ND
10/22/03	BZM-01	Maintenance Mechanic	0.14	969	ND
10/22/03	BZM-02	Maintenance Mechanic	0.14	962	ND
10/23/03	BZP6-1	Activator Operator Plant 6	0.23	1236	Trace
10/23/03	BZP6-2	Chief Operator Plant 6	0.22	1238	Trace
10/23/03	BZP6-3	Plant 6 Reactor #1 Operator	0.25	1188	0.10
10/23/03	BZP6-4	Plant 6 Reactor #1 Operator	0.23	1218	Trace
10/23/03	BZP7-01	Plant 7 Reactor #1 Operator	0.17	1188	Trace
10/23/03	BZP7-02	Chief Operator Plant 7	0.1	767	ND
10/23/03	BZP6-6	Plant 6 Reactor #1 Operator	0.14	1218	ND

An average blank concentration of 0.13 µg/sample was subtracted from the sample results before calculating the 10-hr TWA. Where the 10-hour TWA was <0.03 µg/m³ the results were reported as ND (non-detected). Results between 0.03 µg/m³ and 0.08µg/m³ were reported as Trace.

* This is the total amount of hexavalent chromium collected on the sample media during the sample period.

** The 10-hour TWA was calculated by dividing the sample volume (amount of air) by 1000 to convert to cubic meters, then dividing the lab result by the # of cubic meters. The resulting air concentration was multiplied by the sampled time and then divided by 600 minutes. **The NIOSH 10-hour REL-TWA, Recommended Exposure Limit is 1µg/m³.** Any result listed in this column that is over 1.00µg/m³ will be considered as being over our limit.

Pump faulted.

LOD = 0.04 µg/sample. LOD is the lowest concentration that can be detected above background noise and that is specific to the analytical procedure used.

LOQ = 0.10 µg/sample. LOQ is the lowest concentration that can be quantified with confidence and that is specific to the analytical procedure used

MDC= 0.03 µg/m³. MDC is the minimum detectable concentration for a given a sample volume. The MDC was calculated by dividing the LOD by 1.2 m³.

MQC= 0.08µg/m³. MQC is the minimum quantifiable concentration for a given sample volume. The MQC was calculated by dividing the LOQ by 1.2 m³.

Table 2
Hexavalent Chromium Short Term Exposure Monitoring Results
HETA 2003-0328-2935
CPC Pasadena Plastics Complex
Pasadena, Texas
October 20-24, 2003

Date Collected	Sample#	Task	Lab Result (µg/sample)	Sample Volume (l)	TWA* (µg/m³)
10/20/03	BZP6-06	Chief Operator Plant 7	0.1	98.5	ND
10/20/03	BZP6-07	Chief Operator Plant 6	0.30	98.5	1.7
10/21/03	BZP8-06	Activator Operator Plant 6	0.14	46	ND
10/21/03	BZP8-07	Activator Operator Plant 6	0.12	44	ND
10/22/03	BZP7-05	Activator Operator Plant 6	0.11	48	ND
10/22/03	BZL-01	Laboratory Technician	0.23	66	1.5
10/23/03	BZP6-5	Chief Operator Plant 6	0.27	75	1.9

*The OSHA Ceiling Limit for Cr(VI) as CrO₃ = 100 µg/m³, as Cr(VI) = 52 µg/m³. An average blank concentration of 0.13 µg/sample was subtracted from the sample results before calculating the TWA.

LOD = 0.04 µg/sample. LOD is the lowest concentration that can be detected above background noise and that is specific to the analytical procedure used.

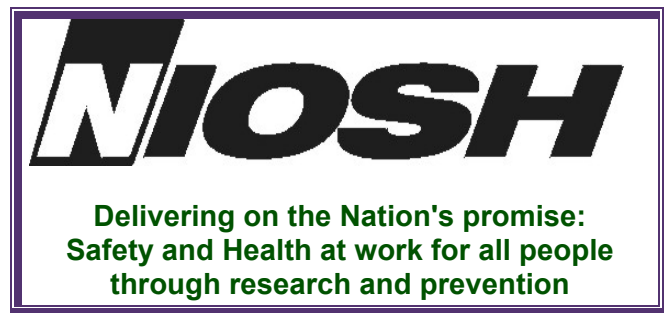
LOQ = 0.10 µg/sample. LOQ is the lowest concentration that can be quantified with confidence and that is specific to the analytical procedure used

MDC = 0.40 µg/m³. MDC is the minimum detectable concentration for a given sample volume. The MDC was calculated by dividing the LOD by 0.1m³.

MQC = 1.0 µg/m³. MQC is the minimum quantifiable concentration for a given sample volume. The MQC was calculated by dividing the LOQ by 0.1m³.

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