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Development of a Standardised Method for Measuring Manganese Exposure

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The aim of this project is to propose a standard or reference method for sampling airborne Manganese (Mn), so Mn exposure levels can be compared between manganese and manganese compound manufacturing from different countries. A systematic literature review was undertaken to identify key references reporting comparisons between aerosol samplers and analytical methods used to assess Mn air exposures and for the more general measurement of dust in workplaces. In addition, information on current samplers used by the industry was collected through a questionnaire which was distributed to the International Manganese Institute (IMnI) members.

The results of the literature review, together with the information collected through the questionnaire survey were presented and discussed with IMnI representatives. The discussion led to the selection of three candidate methods: the IOM head for the inhalable fraction, the Higgins Dewell (HD) cyclone for the respirable fraction and the Conical Inhalable sampler (CIS) for the simultaneous collection of both fractions. The selection was based on following requirements: the samplers should follow the CEN/ISO/ACGIH criteria for collection of inhalable and respirable airborne particles and the sampling medium should not impede the chemical analyses of Mn as well as availability and usability.

The performance of these three candidate methods was compared in four sampling campaigns at four separate Mn production facilities. A standardised sampling survey protocol was developed and followed to ensure samples were collected in a similar way. Parallel personal (CIS vs. IOM or CIS vs. cyclone) and static samples (CIS vs. IOM vs. cyclone) were collected at each facility. The sampling strategy aimed to sample at a spectrum of potential Mn exposures, covering a range of different industrial processes.

A total of 47 paired personal samples (24 CIS-Inhalable: IOM and 23 CIS-Respirable: cyclone) and 65 paired static samples (30 CIS-Inhalable: IOM and 35 CIS-Respirable: cyclone) were collected. Samples collected with the CIS sampler over-estimated the concentrations relative to samples collected with the IOM head (inhalable) and HD cyclone (respirable). The arithmetic mean of the dust ratios CIS-I: IOM was 8.07 and 1.85 for personal and static samples, respectively, whereas the ratio between the CIS-R and the cyclone was 1.91 and 1.76 for the personal and static measurements, respectively. For Mn, the AM ratios were 3.39 and 2.10 for personal and static CIS-I: IOM, and 9.53 and 2.64 for personal and static CIS-R: cyclone.

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It was also observed that the foams used in the CIS sampler contained high Mn levels (blank foams ≈6.03 µg) compared to the low Mn content in the glass fibre filters used with the cyclone (<0.01 µg) and the IOM head (0.22 µg). In addition there was also higher gravimetric instability of the foams relative to the filters, which results in a higher limit of detection (0.1 mg) compared to that for the filters used with the cyclone and IOM head (0.05 mg).

Whilst the CIS sampler offers the advantage of simultaneous collection of both the inhalable and the respirable fractions, based on these results, the IOM head and cyclone were judged to be more appropriate for collection of the inhalable and respirable fraction of Mn compounds.

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ABBREVIATIONS

AAS	Atomic Absorption Spectroscopy
ACGIH	American Conference of Governmental Industrial Hygienists
AES	Absorption Emission Spectroscopy
AM	Arithmetic Mean
CEN	Comité Européen de Normalisation (European Committee for Standarization)
BMRC	British Medical Research Council
CA	Cellulose Acetate
CD	Criteria Document
CE	Cellulose Ester
CIP	Capteur Individuel de Poussiere
CIS-I	Conical Inhalable Fraction- Inhalable fraction
CIS-R	Conical Inhalable Fraction- Respirable fraction
CCOSH	Canadian Centre for Occupational Health and Safety
CYC	Cyclone
GC/MS	Gas Chromatography Mass spectrometry
GM	Geometric Mean
GSD	Geometric Standard Deviation
GSP	Gesamtstaubprobenahme an der Person
HD	Higgins Dewell
HSE	Health and Safety Executive (UK)
IHPAT	Industrial Hygiene Proficiency Analytical Testing
ICP	Inductively coupled plasma
IEH	Institute for Environment and Health
IMnI	International Manganese Institute
INERIS	Institut National de l'Environnement Industriel et des risques
IOM	Institute of Occupational Medicine
ISO	International Standard Organization
LOD	Limit of Detection
MMAD	Mass Median Aerodynamic Diameter
MS	Mass Spectrometry
NIOSH	National Institute for Occupational Safety and Health (US)
OEL	Occupational exposure limit
OSHA	Occupational Safety and Health Administration (US)
PIDS	Personal Inhalable dust Spectrometer
PUF	Polyurethane Foam
REACH	Registration, Evaluation, Authorisation and restriction of CHemicals
RSD	Relative Standard Deviation
SD	Standard Deviation
WASP	Workplace Analysis Scheme for Proficiency
XRF	X-ray fluorescence

SUMMARY

The Institute of Occupational Medicine (IOM) in collaboration with the MRC Institute for Environment and Health (IEH) produced a health Criteria Document (CD) for Manganese (Mn) and inorganic Mn compounds that suggested occupational exposure limit (OEL) for respirable and inhalable Mn of 0.1 and 0.5 mg.m^{-3}, respectively. A literature review on the availability of exposure data identified that different measurements methods for Mn are used throughout the industry, which may lead to different results from the exposure measurements.

The aim of this project is to propose a standard or reference method for sampling airborne Mn, so that Mn exposure levels can be compared between manganese and manganese compound manufacturing industries.

A systematic literature review was undertaken to identify key references reporting comparisons between aerosol samplers and analytical methods used to assess Mn air exposures and for the more general measurement of dust in workplaces. In addition, information on current samplers used by the industry was collected through a questionnaire which was distributed to members of the International Manganese Institute (IMnI).

Results from the review together with information collected through the questionnaires lead to the selection of three candidate methods: the IOM head for the inhalable fraction, the Higgins Dewell (HD) cyclone for the respirable fraction and the Conical Inhalable sampler (CIS) for the simultaneous collection of both fractions. The selection was based on following requirements: the samplers should follow the CEN/ISO/ACGIH criteria for collection of inhalable and respirable airborne particles and the sampling medium should not impede the chemical analyses of Mn.

Concentrations collected with the three candidate sampling methods were compared in four Mn producer sites who volunteered to take part in the field study. A sampling survey protocol was developed to ensure that the execution of the sampling surveys was consistent. The aim was to collect both personal and static exposure measurements, from a variety of jobs and locations and over a wide range of jobs and activities. Samplers were analysed for collection of inhalable and respirable dust and inhalable and respirable total Mn. Details on the locations and job titles to be sampled were determined following a preliminary site visit when possible, or during a phone conference with the relevant personnel at each site.

A total of 332 measurements were considered valid for the comparison exercise. From these, there were 54 paired inhalable measurements (CIS-I vs. IOM: 24 personal & 30 static) and 58 respirable measurements (CIS-R vs. cyclone: 23 personal and 35 static). Measurements with a dust or Mn mass below the limit of detection (LOD) were assigned half value of the LOD.

The three samplers were found to be suitable for occupational hygiene purposes. The samplers were light and did not impose a burden on the wearer and they were easy to operate and clean.

The CIS sampler oversampled in comparison with the concentrations collected with the IOM (inhalable) and HD cyclone (respirable). The arithmetic mean (AM) of the dust ratios CIS-I: IOM was 8.07 and 1.85 for personal and static samples, respectively, whereas the ratio between the CIS-R and the HD cyclone was 1.91 and 1.76 for the personal and static measurements, respectively. For the Mn the AM of the ratios was 3.39 and 2.10 for personal and static CIS-I: IOM, and 9.53 and 2.64 for personal and static CIS-R: cyclone. Differences in the Mn measurements collected with the differences samplers were not significantly affected by sample type (personal or static), process (presence or absence of fumes), percentage of respirable dust

and site. However, the different in dust measurements collected with the CIS-I and IOM were affected by the percentage of respirable dust and site.

The sampling mediums for the three samplers were suitable for analysis of Mn. However, a major disadvantage of the CIS sampler is the high levels of Mn contained in the blank foams (≈6.03 µg, n=2) compared to the low Mn content in the fibreglass filters used with the cyclone (<0.1 µg, n=6) and the IOM head (0.22, n=6). In addition to the higher gravimetric instability of the foams, which results in a higher LOD (0.1 mg) compared to the LOD for the filters used with the cyclone and IOM head (0.05 mg).

The CIS has the advantage of sampling both fractions simultaneously; however results from this study show it consistently overestimates concentrations in relation to those measured with the IOM sampler and HD cyclone, and showed higher LOD for the Mn analysis. The questionnaire survey suggested that the current sampling methods used in most of the Mn industry are the IOM head and cyclone. Therefore, based on these findings it is proposed that the IOM and HD cyclone sampler are used for collection of the inhalable and respirable aerosol fractions of Mn.

1 INTRODUCTION

In 2004, the IOM in collaboration with the MRC IEH produced a health CD for Mn and inorganic Mn compounds (IEH/IOM, 2004). The CD concluded that the respirable dust fraction is the biologically most relevant dust fraction in relation to human health effects and that any exposure limit for Mn should be based on this. However, it was recognised that there may also be some exposure scenarios where the respirable dust fraction is low, but where exposure to larger particles is sufficiently large that exposure via the gastrointestinal tract is not insignificant. To provide additional control for these exposure scenarios, it was also recommended to set a standard for inhalable dust. The CD suggested an occupational exposure limit (OEL) of 0.1 $mg.m^{-3}$ for respirable Mn and a supplementary limit of 0.5 $mg.m^{-3}$ for inhalable Mn.

A literature review on the availability of exposure data in the context of REACH (Registration, Evaluation, Authorisation and restriction of Chemicals) identified that different sampling and analytical methods for Mn are used throughout the industry. This is likely to lead to inconsistencies in the exposure measurements and limit the comparability of available measurement data (Searl, 2007).

The aim of the current study was to propose a standardised or reference method for sampling Mn. A standard method has the advantage of facilitating comparisons between sites, companies and countries, and with appropriate OELs.

To achieve this aim the following objectives were defined:

i. To summarise the main sampling and analytical methods used to measure airborne particles and Mn in air reported in the peer-reviewed literature and provide a discussion on their various advantages and limitations.

ii. To collect information from the Mn industry on current sampling and analytical methods used for measuring exposure to Mn.

iii. To select a set of samplers to measure the inhalable and respirable Mn concentrations with due consideration of the information gathered in i and ii.

iv. To conduct a field comparison of the selected aerosol samplers at a number of Mn producer sites.

The information gathered in these objectives is presented in this report as follows:

Chapter 1:	Description of the aims and objectives of the project.
Chapter 2:	Introductory chapter to dust sampling and a description of common methods available for sampling Mn dust.
Chapter 3:	Summary of the peer-reviewed literature on the performance of the different dust sampling methods.
Chapter 4:	Summary of the information collected from the Mn industry via questionnaire survey.
Chapter 5:	Review of analytical methods for analysis of Mn in airborne samples.

Chapter 6:	Proposal of three candidate methods for collection of Mn across the Mn industry.
Chapter 7:	Field evaluation of the three candidate methods.
Chapter 8:	Final discussion and proposal of a standard method for measuring respirable and inhalable Mn.

2 INTRODUCTION TO AEROSOL SAMPLING

Information on the particle size distribution is important in understanding the potential health effects of exposure to airborne particles. Historically, the sampling of coarse particles for health related purposes was based on the use of sampling instruments for the ‘total’ aerosol fraction. The assumption was that these instruments would sample all sizes of airborne particles with 100 % efficiency. In practice the measurement of ‘total’ aerosol varied greatly depending on the instrument used.

Health related aerosol size fractions are expressed as functions linking the probability of aerosol penetration to the aerodynamic size of airborne particles (Figure 1). The British Medical Research Council (BMRC) definition of the respirable aerosol fraction (those particles with a median aerodynamic diameter of 5 µm collected with a 50 % efficiency) was the first recognized internationally (Orenstein, 1960). In 1989, new criteria for aerosol fractions were proposed by Soderholm (1989) and international collaboration lead to the agreement on the definitions of health-related aerosol fractions in the workplace, defined as inhalable, thoracic and respirable (Figure 1, CEN, 1992; ISO, 1995; ACGIH, 1995). The respirable curve has a median aerodynamic diameter of 4.25 µm and the thoracic curve of 11.64 µm. The inhalable curve has 100% penetration for small particles, dropping to 50% for 100 µm particles and has no median aerodynamic diameter. Each curve can be interpreted as the sampling criterion to be achieved by an aerosol sampling instrument, in order to measure the corresponding aerosol fraction (Görner and Fabriès, 1996).

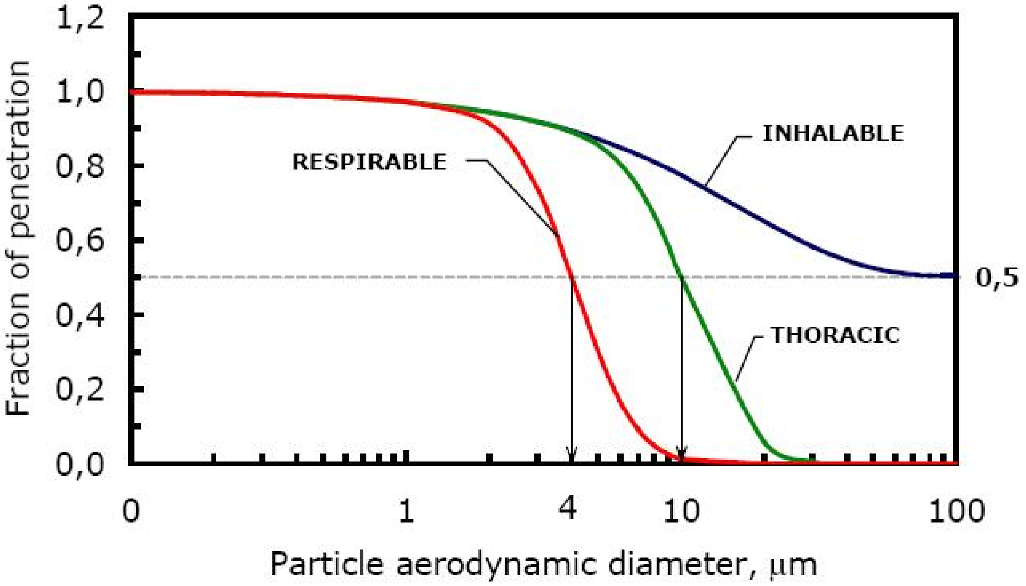

Figure 1 Probability or aerosol penetration as a function of aerodynamic diameter, internationally agreed by CEN/ISO/ACGHI

Several personal samplers designed to collect the ‘total’ aerosol fraction have been re-evaluated in relation to the inhalable criterion including the 37-mm cassette (in their open and closed configuration), multi-orifice (or seven hole) sampler, CIS and the Capteur Individuel de Poussiere 10 (CIP 10) personal dust sampler. Following international agreement on these sampling criteria new samplers have been developed with penetration characteristics that meet the CEN/ISO/ACGIH criteria. For example, the IOM head and button sampler for inhalable dust, and cyclone type samplers for the respirable fraction. Other samplers have been developed that collect multiple fractions simultaneously, such as cascade impactors, the conical inhalable sampler (CIS) and the IOM dual-fraction sampler. Further information on these samplers is provided in the section 3.2.

Numerous studies have been published comparing the performance of different samplers (e.g. Vaughan et al. 1990; Vincent, 1995; Vinzents et al. 1995; Aitken and Donaldson, 1996; Tsai et al. 1996; Wilsey et al. 1996; Kenny et al. 1997; Kenny et al. 1999; Ogden et al. 1997; Demange et al. 2002; Linden et al. 2000; Görner et al. 2001; Teikari et al. 2003). The results from these studies suggest that the use of different samplers can result in significant differences in the observed particle concentration. Wind velocity and direction, inlet size, geometry, orientation, aerosol particle size, electrical charge, particle bounce properties, the sampler conductive properties along with other factors have been identified to affect the performance of samplers (Aizenberg et al. 2001). Further information on the different samplers' performance to the relevant sampling criteria is also provided in the chapter 3 of this report.

The varying performance of different sampling devices causes a degree of uncertainty when using the sampling results to check compliance with regulatory limits, or when the data are used for risk assessment and management purposes.

3 LITERATURE REVIEW

3.1 METHODOLOGY

Two documents the ‘Review of the availability of exposure and toxicological data for manganese and its compounds relevant to the purposes of REACH’ (Searl, 2007) and ‘Occupational Exposure Limits: Criteria document for manganese and inorganic manganese compounds’ (IEH/IOM, 2004) were reviewed in the first instance as these provide excellent summaries of the published literature which provide exposure information related to Mn in air exposures. Those peer-reviewed articles identified as potentially containing information on the sampling and analytical methods used to determine Mn in air exposure were then obtained for further review.

A specific search of the electronic databases including GoogleScholar, PubMed, Canadian Centre for Occupational Health and Safety (CCOSH) OSH Reference and Highwire Press (Stanford University) and specific journals (e.g. Journal of Environmental Monitoring and Aerosol Science and technology) were also undertaken to identify key references reporting comparisons between aerosol samplers and analytical methods used to assess Mn in air exposures and for the more general measurement of dust in workplaces.

3.2 COMMON PERSONAL AEROSOL SAMPLING HEADS

3.2.1 Introduction

Personal monitors are most commonly used to evaluate worker exposure to airborne chemicals. In personal sampling for inhalation exposure, the sampler is attached to the wearer within his or her breathing zone. The breathing zone is the space around the worker's face from where the breath is taken, and is generally accepted to extend no more than 30 cm from the mouth. Personal sampling instruments are normally mounted on the upper chest, close to the collar-bone (HSE, 2000). Although direct reading instruments are available that determine particulate concentration using various techniques, the most commonly used method for determining particulate concentrations is using a gravimetric method. This method involves sampling a known volume of air through a filter. The filters are weighed before and after exposure to determine the mass of particles sampled, which is typically expressed in terms of mass per volume of air sampled (mg. m^{-3}). The collected particulates on the filters can be then be further analyzed for specific components as required, assuming that the filter media used to collect the aerosol sample is compatible with this.

Limited information was available in the peer-reviewed literature on sampling methods used for assessing exposure to Mn in air with the level of detail also being variable. A summary of the methods used is shown in Table 1. Note, a blank cell in the table indicates that this information was not provided in the article.

A variety of sampling heads have been used to assess aerosol fractions including respirable, inhalable and ‘total’. The use of multi-fraction samplers appears to be very rare. The IOM sampling head was most commonly reported when assessing the inhalable fraction and a variety of cyclone samplers have been reported when assessing the respirable fraction. In some cases it was reported that particulates collected in the grit pot of cyclone samplers were analysed to obtain either the ‘total’ or an estimate of the inhalable aerosol fraction (e.g. Bader et al. 1999; Dietz et al. 2001); however this practice is not recommended because of its poor accuracy. When the ‘total’ dust fraction was sampled, this was generally done using a 37-mm cassette.

Details were generally lacking on the sampling medium used, but cellulose acetate (CA) / mixed cellulose ester (CE) filters appear to be most commonly used when reported.

Table 1 Sampling methods used to determine exposure to Mn in air (reported in the peer-reviewed literature)

Aerosol aspect	Sampling head	Sampling medium	Citation
Size distribution	Marple cascade impactors	PVC	Hanley and Lenhart (2000)
	-	PVC	Kawamoto and Hanley (1997)
Total & respirable	Persometer	-	Hlavay et al (1993)
Total	Closed-face cassettes	0.8µm MCE	Hanley and Lenhart (2000)
	-	0.8µm CA	Lucchini et al (1997)
	Zambelli pumps	0.8µm CA	Apostoli et al (2000)
	Midget impinger	-	Emara et al (1971)
	37-mm cassette	-	Lucchini et al (1999) Kominsky and Shulte (1983)
	Casella cyclone filter and grit pot	0.8µm CA	Boojar and Goodarzi (2002) Roels et al (1992) Roels et al (1999)
	25-mm Millipore cassettes (Welding)	5.0µm PVC	Ellingsen et al (2006)
	37-mm Millipore cassette (in line with respirable)	CA	Mergler et al (1994)
	Casella Model C sampler, fitted with holder model T	37mm GF	Roels et al 1987
	-	0.8µm MCE	Kawamoto and Hanley (1997)
	37-mm Millipore cassette	-	Myers et al (2002) Smargiassi et al (2000) Gan et al (1988)
	37-mm type sampler	-	Koudogbo et al (1991) Gibbs et al (1999)
	NIOSH 7300 (37-mm cassette)	NIOSH method 7300 (either PVC or CE)	Korczynski (2000)
	IOM sampler	0.8µm CE (25mm)	Ellingsen et al (2003) Ellingsen et al (2000) Thomassen et al (2001)
Inhalable	IOM sampler	-	Myers et al (2002) Thomassen et al. (2001)
	Casella cyclone filter and grit pot	-	Bader et al. (1999) Dietz et al (2001)
	Modified Lippman cyclones	0.8µm CA (37mm)	Lucchini et al. (1997)
	Grit pot equipped with plastic cup connected to Casella cyclones	-	Roels et al. (1992)
Non-respirable	Lippman cyclone	-	Apostoli et al. (2000)
Respirable	10-mm nylon cyclones	MCE	Hanley and Lenhart (2000)
	Dorr Oliver nylon cyclone	-	Mergler et al. (1994)
	Dorr Oliver nylon cyclone	MCE	Kawamoto and Hanley

Aerosol aspect	Sampling head	Sampling medium	Citation
			(1997)
	York dust sampler	-	Smargiassi et al. (2000)
	25mm SKC cyclone (NIOSH 0600)	MCE	Westberg et al. (2001)
	Casella cyclones (2.2 l/min)	0.8µm CE (37mm)	Ellingsen et al. (2003) Ellingsen et al. (2000) Thomassen et al. (2001)
	Casella cyclones (1.85 l/min)	CE	Roels et al. (1992)
	Casella cyclone (type 13043/1) (fitted with grit pot)	0.8µm CA	Boojar and Goodarzi (2002)
	Midget impinger	-	Smyth et al. (1973)

PVC: Polyvinyl Chloride; MCE: Mixed Cellulose Ester; CA: Cellulose Acetate; CE: Cellulose Ester; GF: Glassfibber

The following sections provide details of common methods used for personal sampling airborne particulates based on the size fraction collected and the physical mechanism to fractionate particles. The information contained within the following sections is based on information provided by sampling head manufacturers websites and the textbook ‘Aerosol Sampling’ by Vincent (2007).

3.2.2 Personal samplers for ‘total’ dust

37-mm cassette (closed- or open-face)

A commonly used ‘total’ aerosol filter holder is the 37-mm cassette (Figure 2). This sampler consists of three-parts, made of conducting plastic. There are two configurations available, the closed-face and open-face cassette.

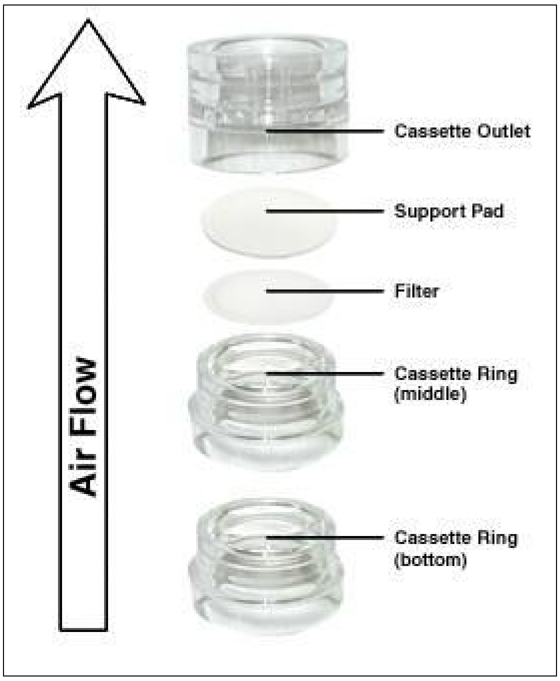

Figure 2 Schematic representation of the 37-mm cassette sampler (source http://www.skcinc.com/prod/filters.asp)

In the closed-face configuration, one part contains a 4-mm diameter sampling orifice that is raised about 2-mm from the flat face of the sampler. The second part has a nipple that enables connection with the tube that leads to the pump and contains a 37-mm diameter filter for particle collection. The third part is inserted between the two other parts, and ensures a firm location of the filter (Vincent, 2007). A small sealing plug is removed from the inlet section during sampling.

The open-faced configuration is a simpler version of the closed-faced sampler. In this arrangement, the first part of the sampler consists of a spacer ring that holds the 37-mm filter, such that the effective sampling orifice is 35-mm. In contrast to the closed-faced design, air is sampled directly onto the filter without passing through the restricted opening (the inlet section of the sampler is not included). A 25-mm version of the open filter sampler has also been used in some European countries (Vincent, 2007).

The sampling flow rate for both configurations is 2.0 $l.min^{-1}$. The 25-mm open-filter version operates at the same flow rate. Both configurations are available from a range of manufacturers, mostly based in USA (Vincent, 2007). It was reported that the closed-face cassette are used for the majority of aerosols since the cassette in this configuration lends protection to the filter and its accumulated contaminant (Beaulieu et al. 1980).

The 37-mm cassette is the recommended method for sampling metals and metalloids by the US Occupational Safety and Health Administration Organization (e.g. OSHA, 1991; OSHA, 2002). Differences between dust concentrations collected with closed- and open-face cassettes have also been observed, with higher concentrations sampled with the open-face configuration. Beaulieu et al. (1980) and Buchan et al. (1986) reported that these differences were due to negative bias of the closed-face sampler against collecting large particles.

3.2.3 Personal samplers for inhalable dust

IOM Inhalable head

The IOM sampler was developed by scientists at the IOM (Mark and Vincent, 1986). The sampler meets the CEN/ISO/ACGIH curve for inhalable dust at a flow rate of 2.0 $l.min^{-1}$ (SKC, Inc., Eighty Four, PA, USA) and is recommended for sampling the inhalable fraction by the UK Health and Safety Executive (HSE) (HSE, 2000).

Figure 3 provides an exploded view of the IOM sampler. The IOM sampling head comprises a cylindrical body, with a cap incorporated at the end with a 15-mm circular orifice having a lip that protrudes 15 mm outwards. The purpose of the lip is to minimize particles deposited on the outer surfaces of the inlet to be carried into the sampler. The cassette incorporates a 25-mm filter. There are two versions of the IOM head, one made of conductive plastic and another of stainless steel. The cassettes are also available in conductive plastic and stainless steel, which although heavier, is less prone to weight changes due to moisture uptake (Paik and Vincent, 2002). The cassette was designed to be weighed together with the filter so any particles deposited on the internal surfaces of the cassette are included in the measurement. It should be noted that weighing the cassette together with the filter leads to higher LODs, compared to weighing only the filter. Therefore, if not very high loadings are expected it may better to weigh only the filter.

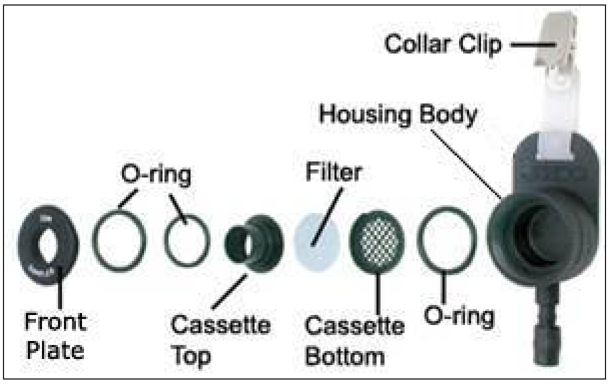

Figure 3 IOM Inhalable head (source http://www.skcinc.com/prod/225-70.asp)

Button Inhalable sampler

The button inhalable sampler is manufactured by SKC and is reported to closely follow the CEN/ISO/ACGHI sampling criteria for inhalable particulate mass at 4.0 $l.min^{-1}$ (SKC, Inc. Eighty Four, PA, US). It has a stainless steel porous curved surface inlet which is designed to improve the collection characteristics of the inhalable dust such that particles are uniformly distributed on the filter (Figure 4). In addition, the streamlined profile of the inlet surface reduces the flow distortion in the vicinity of the sampler and the proximity of the filter to the inlet minimizes losses due to deposition on the walls.

Figure 4 Button sampler (top) and schematic representation of the sampler parts (bottom) (source SKC, Inc., Eighty Four, PA, US)

Conical inhalable sampler (CIS)

The Conical Inhalable Sampler (CIS) (Figure 5) comprises a conical inlet with an 8-mm hole at the top. The inlet is connected to a cassette that holds a 37-mm filter and when worn the orifice faces outwards. The sample flow rate is 3.5 $l.min^{-1}$. The CIS is manufactured as the Gesamtstaubprobenahme an der Person (GSP) sampler by GmgH and Co., Kaarst, Germany and is also available from Casella (Belford, UK) and by BGI. Inc. (Walthman, MA, US). The CIS is recommended for sampling the inhalable fraction by HSE (HSE, 2000), although it is acknowledged that under certain conditions the sampler can exhibit biases (Kenny et al. 1997, 1999).

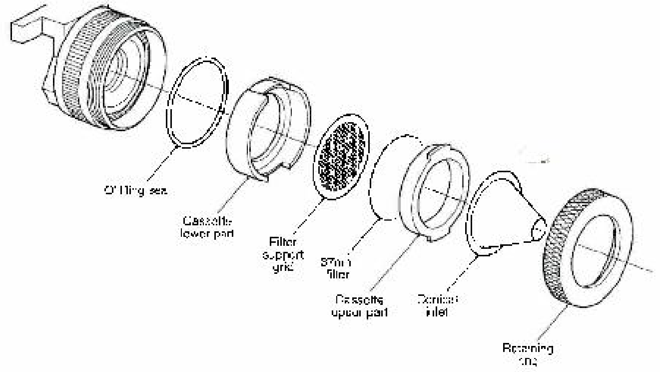

Figure 5 Expanded diagram of Conical Inhalable sampler (HSE, 2000)

Multi-orifice (seven hole) sampler

The multi-orifice sampler, also known as the seven hole sampler, is suggested by the HSE (HSE, 2000) for sampling the inhalable aerosol fraction. The sampler consists of a cover with seven circular 4-mm orifices (Figure 6). Particles entering the holes are collected on a 25-mm filter. The nominal flow rate is 2.0 $\mathrm{l.min^{-1}}$. A version of this sampler with an aluminium cover is available from Casella (CEL, Belford, UK). Another version made of conducting plastic is manufactured by SKC (SKC, Inc. Eighty Four, PA, US). Although the multi-orifice sampler is recommended for sampling inhalable dust, it is acknowledged that the sampler can exhibit biases in some workplace conditions (HSE, 2000).

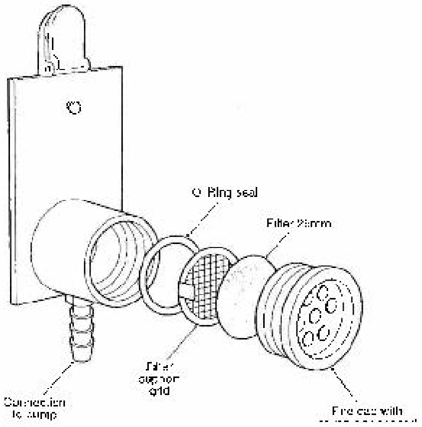

Figure 6 Expanded diagram of multi-orifice (seven hole) sampler (HSE, 2000)

CIP 10

The CIP 10 sampler was originally developed by the French National Institute of the Environmental and industrial risk (Institut National de l'Environnement Industriel et des risques, INERIS) and enables sampling of a specified aerosol fraction depending on the selection of specific size selectors placed on the entry of the rotating cup used (Figure 7). The CIP 10-I (inhalable) operates at a flow rate of 10 l.min^{-1}, and sampling efficiency follows the EN481 (CEN, 1993) and ISO 7708 standards (ISO, 1995) (except for very fine particles).

The sampler includes a rotating cup equipped with polyurethane foam (PUF) mounted on the shaft of the motor turning at high-speed, inside an enclosure that has an axial air inlet and a tangential air outlet. The rotation of the cassette generates airflow by a fan-like effect and assures the capture of the aerosol fraction previously selected by the selector placed upstream of the system. The motor operates on batteries and its speed is set by an electrical control circuit. The flow rate is linearly related to the rotation speed. The air is drawn in through an omni-directional sampling inlet formed by the body of the selector itself and the protective cap. Inside the selector it follows a more or less complex path depending upon the desired particle selection. The selected aerosol fraction next passes through PUF. The particles remaining in suspension after selection are captured and the filtered air is returned to the atmosphere by the tangential orifice of the rotating cup’s enclosure.

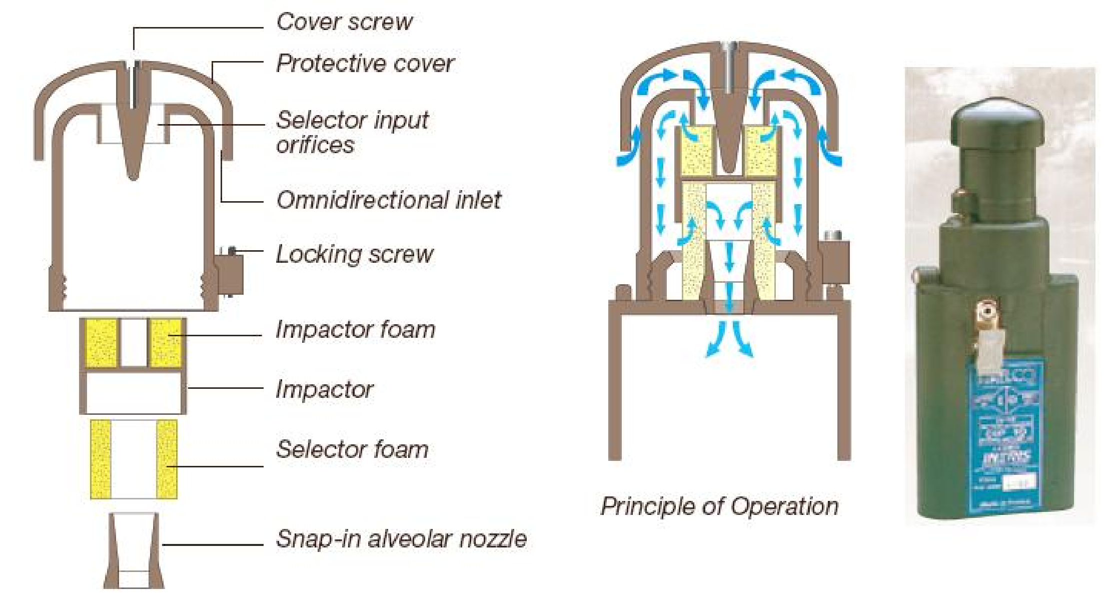

Figure 7 Schematic representation (left) and image of the CIP 10 sampler (Arelco, CIP 10 personal sampler, User’s manual. Fontenay sous Bois Cedex, France)

By using different and appropriate selector foams, the CIP-10 sampler can also be used to assess the respirable fraction (CIP 10-R). The flow-rate is the same as for the CIP 10-I.

3.2.4 Personal samplers for respirable dust

Sampling for the respirable dust fraction is most commonly carried out using a cyclone to separate the respirable fraction from the total aerosol. Cyclone samplers act on the principle of centrifugal force. The rapid circulation of air separates particles according to their aerodynamic diameter. The particle size selectivity of the cyclone and its penetration is achieved by empirical design of the cyclone geometry and selection of specific flow rates. Thus, particles larger than the specified size are forced to the periphery of the air stream, falling into a grit pot and are discarded (Figure 8). Particles of the specified size remain in the centre of the air stream and are drawn onto the pre-weighed filter. The size fraction sampled is very sensitive to variations in the flow rate and deviations from the sampler’s ideal flow-rate may result in significant sampling errors.

In the UK, one the most commonly used cyclones, which is recommended by the Health and Safety Executive (HSE) is the HD cyclone (HSE, 2000). Several versions of the HD design are available, including a modified version known as the SIMPEDS (Safety In Mines Personal Dust Sampler), which was developed for applications in the coal mining. SKC Ltd SKC Ltd. (Blandford Forum, UK) and Casella CEL (Belford, UK) have commercialised HD cyclones made of aluminium or conductive plastic, which are not influenced by electrostatic charges. BGI Inc. (Waltham, MA, US) also commercialised a HD type cyclone made of nickel plated aluminium. The nickel-plate coating has the advantage of reducing the moisture effects observed with uncoated plastic cassettes (Li and Lundgren, 1999). The BGI cyclone uses a push-on filter cassette, in contrast to the Casella and SKC cyclones where the filer is inserted in a screw cap cassette. The aluminum cyclone from SKC operates at a flow rate of 2.5 l.min^{-1} and the conductive plastic cyclone from Casella and the nickel plated aluminum cyclone from BGI Inc operate at a flow rate of 2.2 l.min^{-1}. All these cyclones meet the CEN/ISO/ACGIH criteria. In the USA the most common cyclone is the 10-mm nylon Dorr Oliver cyclone, commercially available from Zefron International Inc. Ocala, FL, USA. The GS-1, commercialized by SKC Ltd. (Blandford Forum, UK) was designed to provide performance equivalent to the Dorr Oliver cyclone, but with the advantage of being constructed in conductive plastic.

A summary of the technical data for the common cyclone samplers is provided in Table 2.

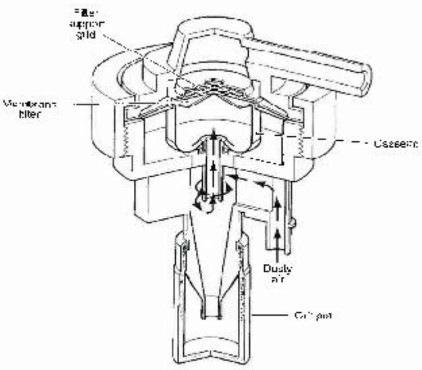

Figure 8 Expanded diagram of a cyclone sampling head (HSE, 2000)

Table 2 Summary of technical data of cyclones

Name	Flow rate (l.min^{-1})	Characteristics and notes
Dorr-Oliver	1.7	10-mm nylon (25 or 37 mm filter)
Higgins and Dewell (original version)	1.9	10-mm nylon
Higgins and Dewell (Casella)	2.2	Conductive plastic
SIMPEDS	1.9	Metal
Higgins and Dewell (SKC)	2.5	Aluminium cyclone (37-mm filter)
Higgins and Dewell (BGI)	2.2	Nickel platted aluminium
GK2.69 (Kenny and Gussman, 1997)	4.2	Aluminium (also available as stainless steel). Can also be used as a thoracic sampler using different flow rate

3.2.5 Multi-fraction personal samplers

Cascade Impactors

Cascade impactors utilize the inertial characteristics of a particle moving in a gas stream to separate the aerosol into different single fractions. Single-stage impactors have a much sharper cut-size (the dividing diameter separating two particle size fractions) than the CEN/ISO/ACGHI convention (Vincent, 2007). Sampling in multiple stages provides a closer penetration characteristic to the CEN/ISO/ACGHI convention. These multi-stage impactors consist of a number of separated plates arranged in parallel with each containing an inlet nozzle, collection plate, and outlet orifice (Figure 9). The diameter of the orifice, the distance between the orifice and the collection plate and the flow rate for each stage are such that a particle greater than a certain size will be separated from the air stream in which it travels, and deposited on the plate. Smaller particles, having less inertia, will remain in the air stream and be carried past the plate. The larger the orifice size and the distance to the plate, the greater is the minimum size sampled. The filters on each plate are weighed separately before and after sampling. Flow rates must be carefully controlled.

Problems associated with impactors include particle bounce and losses on the impaction surface (Vincent, 2007). Collection substrates loaded into the impactors may be pre-greased before use to prevent losses due to particle bounce. Virtual impactors have been developed which differ from conventional impactors in that the impaction surface is replaced by a virtual space of stagnant or slow-moving air where particles can effectively be removed from the flow. The aerosol passes through an accelerating nozzle toward a collection probe. Near the collection probe, a major portion of the airflow is directed away from the probe. Small particles with low inertia follow the flow streamlines and are carried away with the major flow to be deposited on a filter (Figure 10). The larger particles with greater inertia cross the flow streamline and continue moving forward down the collecting probe with the minor flow. The separation efficiency curve is determined by the ratio of the major and minor flows and by the dimensions of the accelerating nozzle and collecting probe (Tatum et al. 2002).

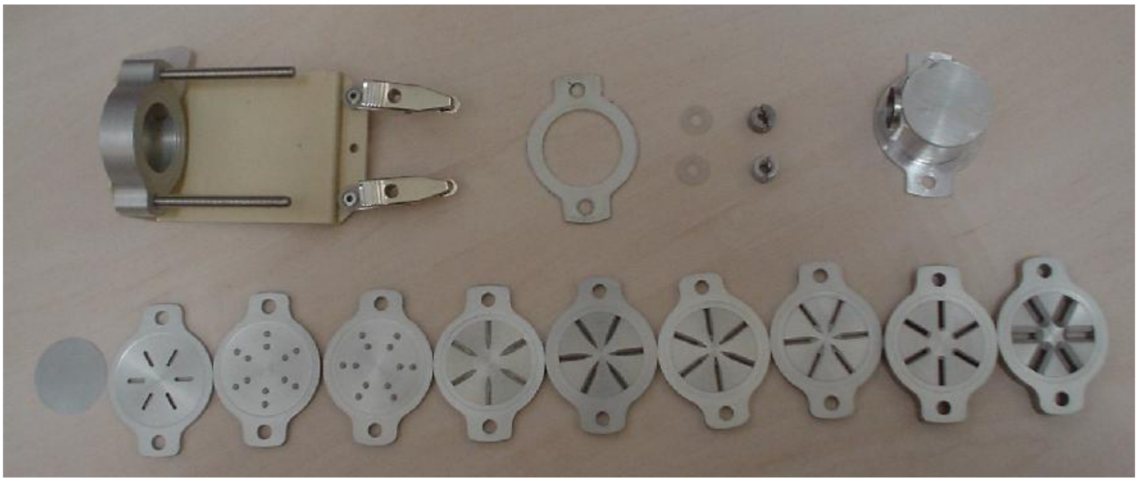

Figure 9 Modified 8-stages Marple cascade impactor (the sampling head has been modified to allow collection of the inhalable fraction)

Various types of cascade impactors are commercially available. For example, the Marple cascade impactor is available in four configurations (2-stage, 4-stage, 6-stage and 8-stage) which allow the user to assess the aerosols particle size distribution between the range of 0.4 and 21 µm (dependent on the configurations used). The head of the impactor can be modified with an IOM inhalable to extend the particle range to the inhalable fraction (Figure 9). The Personal Inhalable dust Spectrometer (PIDS) is similar in concept to the Marple impactors although the slot-shaped impactor jets of the Marple device are replaced by circular jets. Cut-off points in the eight stages of the PIDS range from 0.9 to 19 µm at 2.0 $l.min^{-1}$ (Ruzer and Harley, 2005). The Sioutas Cascade Impactor (SKC. Inc., US) separates and collects airborne particles in five size ranges: > 2.5 µm, 1.0 to 2.5 µm, 0.50 to 1.0 µm, 0.25 to 0.50 µm, and < 0.25 µm at 9.0 $l.min^{-1}$. This makes the device useful when sampling at low aerosol concentrations.

Respicon cascade impactors are commercially available from TSI Inc. (St Paul, MN, US) (Figure 10 and 11). These are available either as an optical or gravimetric version. The gravimetric version consists of three virtual impactors. The impactor operates differently from other impactors, with fine particles being collected first and coarse particles collected on the subsequent stages: at Stage 1, 2.66 $l.min^{-1}$ of the flow is diverted and most particles under 4 µm in diameter are collected on the Stage 1 filter. The remaining particles pass to the second virtual impactor (Stage 2), which diverts 0.33 $l.min^{-1}$ of the remaining flow and collects most particles smaller than 10 µm in diameter onto a filter. The remaining flow of 0.11 $l.min^{-1}$ carries the larger (remaining) particles onto a final filter (Stage 3). The thoracic fraction is the sum of the mass of the first and second filters and the inhalable fraction is the combined mass of the three filters.

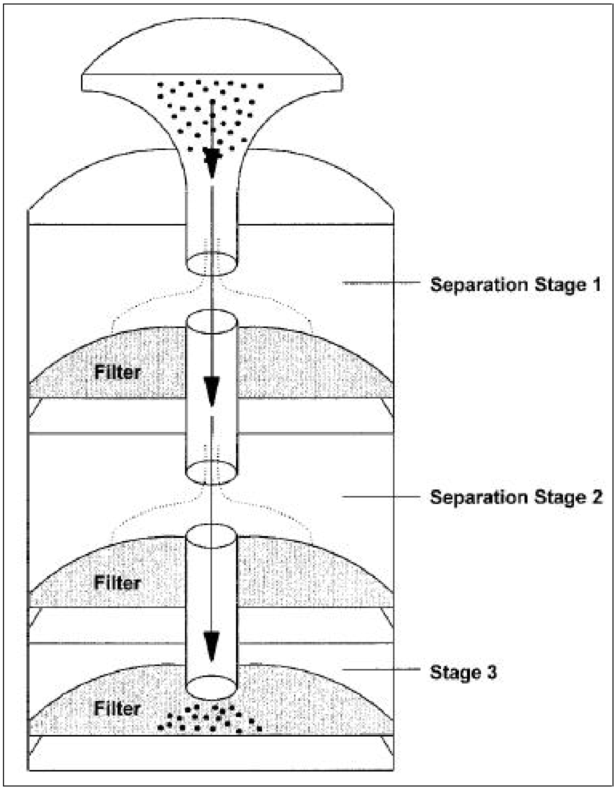

Figure 10 Schematic representation of the Respicon virtual impactor (source: Tatum et al. 2002)

Figure 11 Image of the gravimetric version of the Respicon (source: Koch et al. 2002)

The optical version is identical but with a system of miniaturised photometers at each stage to provide direct reading of the three health-related fractions. Laboratory tests have shown that the sampling efficiency in both versions follow quite closely the ISO/CEN/ACGHI inhalable criteria (Koch et al. 1999; Li et al. 2000). However, the manufacturer recommends application of a correction factor of 1.5 when calculating the inhalable fraction to account for under-sampling of very large particles.

Porous plastic foam filter samplers

The key feature of foam media is the slow penetration changes with particle size, which make them ideal for size-selective sampling. The porous material whose aerosol penetration characteristics have been studied extensively is PUF and this is increasingly being used as a particle size-selective medium for dust sampling applications (Aitken et al. 1993; Chung et al. 1997; Fabriès, 1998; Chen et al. 1998). The key advantage of such samplers is that they can be used to measure multi fraction concentrations in a single sampler.

IOM dual sampler

Foam inserts of specific porosity can be placed into the inlet of the cassette of a standard IOM personal inhalable dust samplers, where they separate the inhalable dust into thoracic and/or respirable sub-fractions. For example, using foam with a specific porosity for the respirable fraction allows respirable particles to be collected on the filter placed at the back of the cassette, with the inhalable aerosol fraction being determined by weighing the foam and filter in combination.

Figure 12 provides a schematic diagram of the IOM sample head with foam insert. Different foam inserts of specific porosity are available which can be placed into the inlet of the cassette of the IOM inhalable dust sampler. The respirable foam plugs are 12 mm thick, 16.5 mm in diameter, and are made with PUF having a cell diameter of 420–460 mm (that is a nominal porosity of 85–90 pores per inch). The sampler continues to be run at a flow rate of 2.0 l.min^{-1}. The sampler is available from SKC, Inc. (Eighty Four, PA, US).

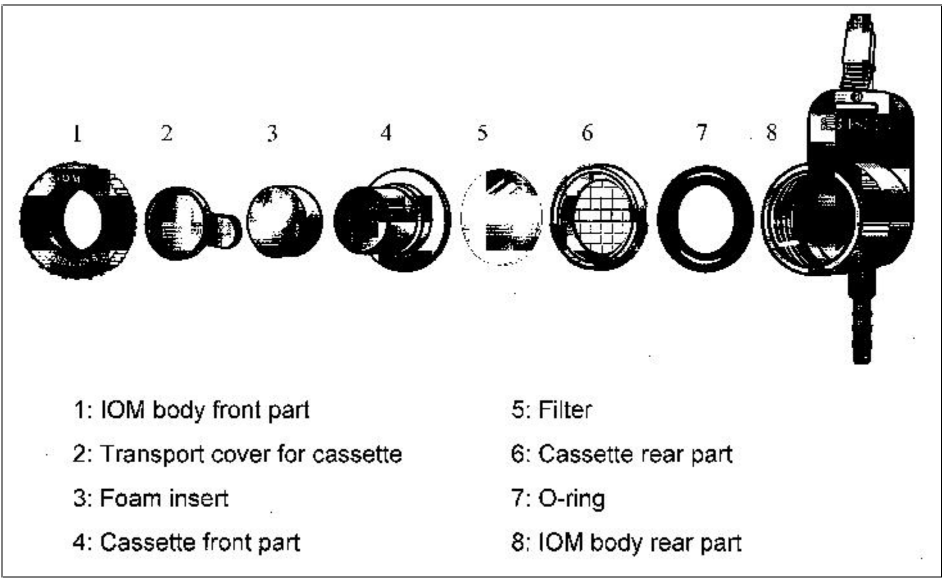

Figure 12 Schematic diagram of the IOM dual fraction dust fraction (Kenny et al.1999)

It is noted that only IOM sampling heads manufactured after June 2000 are suitable for use with the foam inserts. Kenny et al. (2001a) reports that the foam inserts were generally easy to use, and the IOM dual-fraction sampler as a whole compared favourably with the usability of a respirable cyclone and provided a valid alternative method to the respirable cyclone.

Kenny et al. (2001a) reported issues concerning the use of stainless steel cassettes which were expensive, had a high tare weight and were difficult to join and separate without damaging the filter and their were also foam-displacement issues. However these issues appear to have been resolved, with the manufacturer of the IOM sampler (SKC, Inc. (Eighty Four, PA, US) now producing an elongated nickel-plated plastic foam cassette which is lighter, reduces problems of moisture uptake and with the two parts being able to separate without twisting, thus minimising filter damage. Kenny et al. (2001a) also reported internal movements of particles from the filter to the foam during postal dispatch. Particle loss from thoracic foams can be minimised by coating the foam with a solution of Vaseline in xylene. This has been reported to reduce losses from 55 % to 7.5 % of dolomite dust (Rob Aitken, personal communication).

Kenny et al. (2001a) did not encounter any major issues with loading effects on the foams exposed to a variety of airborne substances including silica dust, metal dust, metal fumes and man-made fibres. However, other researchers did observe significant loading effects. Stancliffe and Chung (1997) observed a linear decrease in sampling efficiency with increasing loading of fume, with a magnitude of 1 µm for each 1 mg of fume loaded. De Vocht et al. (2008) also reported loading effects with increasing concentration of clay particles in the dust matrix. Therefore, the potential for loading to degrade the performance of the foam inserts, particularly when very fine particles or long chain agglomerates are collected, should not be ignored.

In addition to potential loading problems of the size selective foams, Kenny et al. (2001b) highlighted possible inter-batch variation in porosities that can cause changes in the cut-off values. However, Kenny et al. (2001a) and Bogdanovic et al. (2006) reported small differences for respirable and thoracic foams, concluding that the effects on the cut-off size are likely to be negligible.

MDHS 14/3 highlights that unless the environmental conditions (air temperature and humidity) are carefully controlled during weighing, large weight variations of size selective foams may be observed due to moisture absorption (HSE, 2000). Washing the PUF with detergent reduces the weight variability and also removes impurities up to a 1 % of the total weight (Rob Aitken, personal communication).

Digestion of the previously washed PUF in concentrated nitric acid resulted in impurities of tin, magnesium and calcium; other elements could not be detected (Aitken, personal communication). Diller et al. (2007) also reported high levels of tin and also platinum in pre-washed PUF digested in nitric acid and hydrogen peroxide, followed by chloric acid and fluoric acid digestion. The high concentration of tin, interfered with the isotope 114 of cadmium, the most commonly used in Ionization Couple Plasma- Mass spectrometry (ICP-MS) analysis. However, no issues were raised regarding the analysis of Mn. Diller et al (2007) found Mn concentrations in the pre-washed blank foams of 8.1 ng per foam, which is below the allowed metal concentration in blank substrates recommended in the ISO protocol for analysis of metals in particulate matter (0.1 µg per foam) (ISO 15202-1:2000).

Porous foam size selectors for the Conical Inhalable Sampler

Foam inserts are available for the conical inhalable sampler (CIS) which are porous to $PM_{2.5}$, PM_{10} or respirable dust (available from BGI Inc). Kenny and Stancliffe (1997) report on a study where cassettes for incorporating foams to sample for aerosol fractions such as $PM_{2.5}$, PM_{10}/thoracic, respirable were tested within an air chamber within the cone of the CIS. At the time of reporting it was emphasised that little practical experience of field sampling with these foam samplers had been obtained and that some refinement of procedures was likely to be necessary in the future.

3.3 COMPARISON OF AEROSOL EXPOSURE METRICS AND SAMPLING METHODS

3.3.1 Introduction

Any interpretation or comparison of findings from Mn exposure studies has to take into account the measurement and analytical methods used, the different size fractions used (inhalable, respirable and ‘total’) and the varying relationships between these.
Comparison of size fractions

The Mn health CD (IEH/IOM, 2004) indicates an inhalable:’total’ ratio of 1.2–3.2 : 1 and a respirable:’total‘ ratio of 0.1–0.5 : 1. The only published study comparing inhalable and respirable fractions is that of Ellingsen et al. (2003) in alloy production, in which the respirable fraction was 0.106 of the inhalable (ranging from 0.074 in product handing to 0.391 in furnace room crane operators). However, the authors of the CD indicated that no simple conversion factors are available as these will be highly and intimately dependent on the aerodynamic size distribution of the sampled aerosol, which vary in different workplace environments. Development of conversion factors requires a detailed understanding of the process leading to the exposure. The authors therefore conclude that ‘in practice the ratio between inhalable and respirable in any given occupational scenario can only be well described by good understanding of the particle aerosol size distribution (which is seldom available) or by use of a multi-fraction sampler or a programme of side-by-side measurements’.

3.4 COMPARISON OF SAMPLING DEVICES

Few published studies of comparative sampler performance have specifically considered Mn. Therefore, the review comparing various sampling devices has been expanded to consider other exposures. This section focuses predominately on the comparison of samplers used to collect the inhalable and respirable aerosol fractions although there is some discussion on the comparison of samplers for collection of ‘total’ dust. A review on the different conversion factors between samplers is also included.

3.4.1 Comparison of ‘total and ‘inhalable’ samplers

The IEH / IOM (2004) report provides an excellent summary of the main studies which have focused on sampling differences between IOM samplers (inhalable) and 37-mm cassettes (total) and these have been summarised further in Table 24.

The ‘total’/inhalable dust ratios tend to increase with increasing particle size (Linden et al. 2000) and wind speed (Kenny et al. 1997a). It was also reported that when particles deposited on the wall of the ‘total’ sampling cassette were recovered and weighed with the mass deposited on the filter, ratios approach to one (Demange et al. 2002).

Overall, it is widely recognised that concentrations measured by the IOM and 37-mm sampling heads will not be equivalent owing to differences between their sampling efficiencies. The IOM head measures apparently higher levels in almost all cases with the difference being dependent on the particle size distribution. The 37-mm cassette losses are mostly due to particle deposits on walls, which will depend on the electrostatic charge of both cassettes and particles, the nature of the filter and air humidity (Demange et al. 2002). Therefore, particle losses are specific for dust type and environmental conditions.

Table 3 Correction factors reported by IEH / IOM (2004) for literature investigating the ratios of the concentrations between IOM sampler and 'total' cassette samplers

Samplers	Ratio	Study characteristics	References cited in IEH/IOM, 2004
IOM / 37-mm closed faced	1.2-1.7	Laboratory	Ogden et al. 1997 ACGIH, 1999 Lidén et al. 2000 CEN, 1992
	3.0	Wood work industry	Vinzents et al. 1995
	2.96	Oil mist aerosols	Wilsey et al. 1996
IOM / 37-mm open faced	1.15	Wind tunnel Con range: 200-300 μg.m^{-3} Particle size: 7-100 μm wind speed 0.5 ms^{-1} 37-mmm flow rate (2 l.min^{-1})	Kenny et al.1997
IOM / 37-mm cassette (configuration not specified)	1.38-4.01	Ni industry	Tsai et al. 1995, 1996 Tsai and Vincent, 2001
	1.51	Bronze foundry	Demange et al. 2002
IOM / 37-mm cassette	1.2–3.0	Nickel refining	Werner et al. 1996

3.4.2 Comparison of Inhalable samplers

Generally sampling performance test are carried out in wind tunnels with the sampler attached to a manikin, which is rotated with respect to the wind direction to simulate workplace ventilation conditions. This setting makes it hard to achieve a uniform wind speed and particle concentration near the sampler zone, resulting in a high variability on the results (Kenny et al. 1997; Aizenberg et al. 2000), and therefore, derived correction factors would have a large degree of uncertainty. In 1997 a full European standard was developed by one of the CEN working groups to evaluate the performance of inhalable samplers in laboratory tests and this was finally approved in 2002 (EN 13205). However, it was considered that samplers should also be evaluated under real workplace conditions. This led to the development of a new protocol system (CALTOOL) to evaluate inhalable sampler's performance in field environments (Mark et al. 2003).

Kenny et al. (1997) examined the performance of the IOM inhalable sampler, multi-orifice, CIS (GSP) and CIP-10 I samplers in a laboratory setting. The tests showed equivalent concentrations at low wind speeds (0.5 m.s^{-1}) between the IOM, multi-orifice, CIS (GSP) and 37-mm close face cassette. The sampling efficiency of the CIP-10 I was found to decrease more rapidly than the CEN/ISO/ACGIH curve. Therefore, a correction factor of 1.15 with regard to the IOM sampler would be needed for the CI-10 I. The 37-mm open face cassette also was found to under sample and would need a correction factor of 1.15. The sampling efficiencies of all samplers decreased with increasing wind speeds. At wind speeds of 1 m.s^{-1} only the IOM and CIS (GSP) met the inhalation criteria and the other samples started to under-sample. At high wind speeds (4 m.s^{-1}) all samplers under-sampled. Kenny et al. (1997) also noted that the sampling efficiency of the IOM sampler decreased at large particle sizes. Deposits on the walls of the cassette increased from zero at small particle sizes to 25 % at 100 μm for a wind speed of 1 m.s^{-1}. For wind speeds of 0.5 m.s^{-1} the efficiency of the IOM sampler agreed with the CEN/ISO/ACGIH curve.

The multi-orifice sampler had previously been shown to under-sample compared to the IOM sampler and CIS (GSP) sampler, with a mean ratio IOM/ multi-orifice of 1.3 (Vaughan et al. 1990) and CIS (GSP)/multi-orifice of 1.7 (Davies et al. (1999). Searl (2000), in a study in UK coalmines also noticed higher concentrations measured by the IOM sampler compared to the multi-orifice sampler.

Further studies have shown that the CIS (GSP) under-samples the inhalable dust concentration compared to the IOM sampler, with greater differences for larger particles in laboratory studies (Kenny et al. 1999: Aizenberg et al. 2001) and field studies (Thorpe et al. 2007).

Aizenberg et al. (2001) compared the IOM sampler, CIS (GSP) and button sampler using two test protocols; one similar to that use by Kenny et al. (1997) and a simplified protocol. Results showed that the IOM sampler matched the inhalable sampling curve well, whereas the sampling efficiencies for the CIS (GSP) sampler and the button sampler fell below the inhalable convention, leading to lower masses being collected on filter. However, the sampling efficiency of the IOM sampler was largely dependant on wind velocity and particle size, as Kenny et al (1997a) had demonstrated earlier. Sampling efficiencies were above 100% for particles of 165 and 241 µm mass median aerodynamic diameter and wind speed of 1 m.s^{-1}. High winds can lead to blow particles directly into the sampler, which orifice has a 1.5 cm diameter. This contrasts with results observed by Kenny et al. In Kenny et al. study it was reported a decrease in the sampling efficiency of the IOM sampler with increasing wind speed as particles are deposited in the walls of the cassette. If the dust measured includes the filter and the cassette deposits then, the sampling efficiency will increase with the wind speed, however if only the dust deposited on the filter deposited is included in the analysis the sampling efficiency will decrease. In Aizeberg et al. paper it is not clear whether they analysed the dust deposited in the cassette and filter or only that deposited on the filter.

The wind effect observed in the IOM sampler was not statistically significant for the CIS (GSP) and button sampler. In contrast, Kerr et al. (2002) in field experiments in the carbon black industry, found no differences between the CIS (GSP) and IOM samplers, possibly because of the small particle sizes of black carbon particles.

Similar results to those obtained by Aizenberg et al. (2001) were observed by Linnaimaa et al. (2008) in a comparison study on a field site with metal and mineral dust. The button sampler under-sampled compared to the IOM sampler, although the differences were not statistically significant. Results in calm wind conditions in a laboratory test resulted in similar results for both samplers.

In 2003, a calibration tool known as CALTOOL was developed as a standard to test inhalable dust samplers for the CEN/ISO/ACGIH sampling criteria. CALTOOL consist of a simplified full-scale mannequin with a ‘mouth’ inlet: the head is mounted on an idealised stainless steel upper torso of elliptical cross section upon which candidate personal samplers are mounted (Mark et al. 2003). Bias calculations showed that, for the particle size distributions recommended in EN 13205 for inhalable aerosol samplers, the results from the CALTOOL were always within + 9% bias of the ideal sampler. The mannequin was tested in several industrial settings. Results from the combination of all tests showed the following ratios of the different samplers against CALTOOL: 1.33 (IOM), 1.06 (Respicon), 1.24 (CIS - GSP), 0.50 (37-mm open face cassette), 0.77 (37-mm closed face cassette), and 0.63 (Button sampler). Further analysis with the IOM and Respicon samplers showed that the IOM sampler exhibited an increase in the IOM:CALTOOL ratio with decreasing particle size and proximity to the source, although results were only statistically significant in the case of particle size. Results from the Respicon (after applying a correction factor based on information about the actual particle size distributions) showed a statistically significant increase in the Respicon:CALTOOL ratio with proximity to the source but not with particle size. The authors found large variability on the results of sampling performance, suggesting that repeated sampling should be carried out.

De Vocht et al. (2006) used the CALTOOL mannequin to compare the performance of various inhalable samplers including the IOM sampling head, the 7-hole sampling head and 37-mm cassette, in four rubber manufacturing factories across Europe. This study involved a wide range of exposure levels and wind speeds and the results shown that the IOM sampler had a performance ratio that did not differ significantly from the CALTOOL device. The 7-hole sampler, and 37-mm cassette, under-sampled the inhalable dust, however, the IOM sampler over-sampled with large particles.

Witschger et al. (2004) designed another protocol for measuring the sampling efficiency of inhalable samplers in close proximity to the source and with low air movement. Measurements from this design compared well with those obtained using the CALTOOL mannequin in similar test conditions. Wichcher et al. tested the performance of the IOM head, button sampler and 25-mm closed-cassette for collection of aluminium oxide powders of 6.9 and 76.9 mass median aerodynamic diameter (MMAD). The IOM sampler demonstrated good agreement with the CEN/ISO/ACGIH inhalablity curve. The authors observed that particle deposition on the IOM metal cartridge was high and particle dependant, increasing from 20% for particles of 6.9 µm MMAD to 55% for particles of 76 µm MMAD. However, provided the cassette is weighed as intended this should not bias the end result.

Some studies have reported slight differences in the concentrations sampled with the IOM sampler (original sampler) and the IOM foam sampler. For example Linnainmaa et al. (2008) observed the IOM foam sampler (for respirable dust) yielded higher concentrations of metal and mineral dust than the IOM sampler without the foam insert. In contrast, Bogdanovic et al. (2006) (using the CALTOOL mannequin to compare both samplers) reported lower concentrations with the IOM foam sampler than with the IOM sampler without the foam for high concentrations (33.2-53.0 mg.m^{-3}) of wheat flour. At lower concentrations both samplers collected similar concentrations. Despite these discrepancies the differences reported between both IOM samplers by Linnainmaa and Bogdanovic were not statistically significant.

Few studies were found in the literature review on the performance of cascade impactors compared to other inhalable samplers. The "entry" for the standard Marple sampler as supplied by the manufacturer, does not meet the criteria for an inhalable dust sampler (CEN, 1993) and would result in an under-estimation of the size fraction of the larger airborne particles (approximately 20 µm and above). Unpublished studies by the IOM have used cascade impactors using a modified inlet designed to collect inhalable dust fraction in accordance with the inhalable dust convention (CEN, 1992) (Hughson, 2005; Creely and Aitken, 2008).

Most of the reviewed studies on the comparison of the performance of the gravimetric version of the Respicon sampler to collect the inhalable fraction with the IOM sampler have shown lower concentrations for the Respicon. Koch et al. (2002) compared the Respicon and the IOM sampler in a nickel refinery as part of the CALTOOL programme. Results showed consistently lower concentrations for the Respicon compared to the IOM sampler. Although the authors indicated that an empirical correction factor could be applied to the Respicon. Similar results were reported by Thorpe (2007) using also the CALTOOL mannequin in a wind tunnel with different sizes of aluminium oxide, Teikari et al. (2003) in a laboratory and field study for sampling of mineral dust and Braveit et al. (2004) in a study of exposure to sulphuric acid in zinc production industry. Rando et al. (2005) reported that the ratio of measured concentrations using the IOM versus the Respicon samplers was 1.23 for sampling of wood dust. Brouwer et al. (2006) also reported that the Respicon sampler underestimated the inhalable fraction compared to the IOM sampler for collection of aluminium oxide, calcium carbonate and magnesium stereate in a simulated workplace study. Pater et al. (2002) also found higher concentrations sampled with the IOM foam sampler and CIS (GSP) compared to the Respicon in a field study with flour dust. However, they observed some problems on the performance on the flow checker of the Respicon. Problems fitting the respirable foams in the IOM head were also reported.

On the other hand, Li et al. (2000) reported that the Respicon efficiency was less influenced by wind speed, direction and particle size compared to the IOM sampler, button sampler, CIS, and 37-mm closed-faced cassette. Comparison of the gravimetric version of the Respicon with the CIS (BGI) sampler for the inhalable fraction in a forest product industry did not show significant differences between both samplers (Tatum et al. 2002)

Berlinger et al. (2007) in a study of metal exposure (total Mn, chromium, copper and nickel) in welding fumes, found slightly higher metal concentrations sampled with the CIS (used without the PUF) than with the IOM sampler, although the differences were not statistically significant.

Development of a generic correlation factor for other inhalable samplers relative to the IOM sampler would be difficult to implement due to the different factors influencing sampling efficiency, particularly the differences in particle size distribution in different workplace environments. Table 4 summarizes the different correction factors found in the literature relative to the inhalable mass sampled with the IOM head. When more than one correction factors was calculated for different wind speeds, those calculated for low wind speeds are reported, since they are more representative of the work environment conditions.

Table 4 Correction factors reported in the literature reviewed for inhalable samplers

Samplers	Ratio	Study characteristics	References
IOM / multi-orifice	1.3	23 different industrial settings	Vaughan et al. 1990
IOM / multi-orifice	1.0	Wind tunnel Con range: 200-300 µg.m^{-3} Particle size: 7-100 µm wind speed 0.5 ms^{-1}	Kenny et al.1997
IOM / Button sampler		Simplified Test protocol (65 µm particles, 4 inlet orientations)	Aizenberg et al. 2000
IOM / CIS (GSP)	1.0	Wind tunnel Con range: 200-300 µg.m^{-3} particles 7-100 µm wind speed 0.5 ms^{-1}	Kenny et al. 1997
IOM / CIS (Casella) (analysis of Mn)	0.96	Welding fume	Berlinger et al. 2007
IOM / CIP 10-I	1.15	Wind tunnel Con range: 200-300 µg.m^{-3} particles 7-100 µm wind speed 0.5-4 ms^{-1}	Kenny et al. 1997
IOM / Respicon	1.83	Ni refinery	Koch et al. 2002
IOM / Respicon	> 1	Mineral dust	Teikari et al. 2003
IOM / Respicon	1.23	Wood dust	Rando et al. 2005
CIS / multi-orifice	1.7	Lumber mill	Davies et al. 1999

3.4.3 Comparison of Respirable samplers

Performance of cyclones for sampling of respirable dust is sensitive to the flow-rate. Optimal flow-rates have been reported for several cyclones. For example Lidén and Kenny (1991) suggested an optimal flow-rate of 2.1 $l.min^{-1}$ for the Casella plastic cyclone, although Görner et al. (2001) found that a nominal flow-rate of 1.9 $l.min^{-1}$ satisfied the CEN (1992) curve for this cyclone. In the case of the SKC aluminum cyclone, Görner et al. (2001) found an optimized flow rate of 2.1 $l.min^{-1}$ whilst for this flow rate Gudmundsson and Lidén (1998) reported a D_{50} of 5.3 µm. Chen et al. (1999) reported an optimal flow-rate of 2.7 $l.min^{-1}$ for the SKC aluminum cyclone. For the Dorr-Oliver nylon cyclone Chen et al. (1998) and Görner et al. (2001) both found an optimized flow rate of 1.5 $l.min^{-1}$ instead the nominal flow rates of 1.7 $l.min^{-1}$.
Optimization of the slope of the sampling curve is not possible by flow-rate modification. It would be necessary to re-design the cyclone. However, some samplers with geometries different from that of the conventional efficiency curve can sample the respirable fraction as long as the over-sampling of fine particles, compensate for the negative mass bias (Görner et al. 2001). However, this could be a source of error when sampling metal concentrations, since the metal content of both fractions may not be the same. For example finer particles have been found to have a higher metal content than larger particles (Thomassen et al. 2001).

Kenny and Gussman (1997) argued that the performance of samplers should be evaluated from the bias and accuracy of the mass sampled rather than from the comparison of the slope and D_{50} of the sampler with those from the sampling convention, because of potential reciprocal compensation depending on the particle size distribution of the sampled aerosol.

Görner et al. (2001) found a smaller uncertainty (experimental cut-off point and slope of the sampling efficiency curve) of the sampled aerosol fraction for the Dorr-Oliver, SKC and Casella plastic cyclones compared to that for the SKC aluminium.

Several authors have compared the results for respirable dust from the IOM foam sampler with other respirable samplers. Kenny et al. (2001) in a study at different industrial settings (including silica dust, mineral fibre, metal dust and fume) did not found statistically significant differences in the concentration of respirable dust measured by a variety of cyclones and the IOM dual-fraction sampler. The regression slope between the IOM sampler and cyclones was 0.93 and the regression coefficient of R^2=0.8. In contrast, a study by de Vocht et al. (2008) in the brick manufacturing industry found a ratio between the HD cyclone/IOM of 1.9, and R^2=0.77 for sampling of silica dust. The correlation decreased as the concentration of clay particles increased. The authors concluded that the performance of the IOM foam sampler depends on the relative concentration of clay particulates in the dust matrix. Linnainmaa et al. (2008) reported that the IOM foam sampler for respirable dust under-estimated the respirable fraction with high dust loads (4 mg per sample).

3.5 SUMMARY

The reviewed studies assessed the samplers' performance using a large range of different methods, which makes difficult to compare results from different studies. However, despite these limitations most of the studies agreed on their general conclusions.

The following inhalable samplers have been designed to meet the ISO/CEN/ACGHI criteria: the IOM inhalable sampler, CIS (GSP), SHS, the button sampler and gravimetric version of the Respicon. However, comparison studies carried out with the calibration tool CALTOOL, developed to test samplers for the ISO/CEN/ACGHI criteria showed a better sampling efficiency for the IOM inhalable sampler compared to the Respicon (Koch et al. 2002, Thorpe et al., 2007) and SHS (Vocht et al. 2006). The CIS (GSP) sampler has shown to under-sample relative to the inhalable convention (Kenny et al. 1999, Aizenberg et al. 2001 and Thorpe et al. 2007). Fewer studies have been performed with the button sampler. Aizenberg et al. (2001) showed good agreement of the button sampler with the inhalability convention whereas Witschger at al. (2004) showed a good performance.

Most of the reviewed literature considered the IOM sampling head as the standardised method for sampling the inhalable aerosol fraction, with the sampler being run at 2 $l.min^{-1}$. The IOM sampling head samples to the inhalable criterion, is recognised by regulatory bodies, including the UK HSE, can be used with any filter medium required and is also easy to use, freely available and widely used.

Results from the comparison between different cyclones for collection of respirable dust have shown that these devices are largely influenced by the sampling flow-rate. All things considered, providing the cyclones have been tested to assure they follow the respirable convention the available literature suggests that there are few differences between the cyclone sampling heads available. However, taking into consideration that there are differences in flow rates and also how the filters are inserted into the sampler it is possible that certain cyclones may be more suitable on HD type cyclone reportedly has the best global acceptability and it is the most widely used to measure the respirable fraction.

The IOM and CIS samplers also have the added benefit that, through the incorporation of PUF, can be used to sample both the inhalable and respirable fractions simultaneously. This would be clearly advantageous to the Mn industry given that both fractions can be assessed without the wearer being required to wear two pumped sampling devices. However, it is acknowledged that the use of the IOM head and CIS, combined with the foams, has not been readily adopted by industries and that further work would be necessary to validate the use of the foam sampler for Mn analysis.

4 INFORMATION FROM THE MN INDUSTRY

4.1 INTRODUCTION

Information on the sampling and analytical methods used to measure Mn exposure as well as contextual information on the exposure surveys were collected via a questionnaire survey administer among the IMnI member companies.

4.2 METHODOLOGY

A questionnaire was developed by IOM and circulated to IMnI for comment. The final agreed questionnaire (Appendix 1) consisted of five sections:

- Section 1: *Background information*. This section includes questions aimed at obtaining information on the industrial sector for the particular site, the number of employees working at the site and those potentially exposed to Mn.
- Section 2: *Manganese in workplace air sampling and analytical methods*. This section includes questions aimed at identifying the type of Mn aerosol sampling undertaken, the sampling heads, medium and analytical methods used.
- Section 3: *Measurement collection and why measurements are made*. This section includes questions aimed at identifying the number of measurements undertaken, who carried out the survey and the sampling strategy employed.
- Section 4: *Manganese exposure information*. This section aims to identify how frequently key contextual information is recorded during workplace air sampling and how exposure measurements are stored.
- Section 5: *A standardised method for measuring Mn exposure.* This section allows respondent sites to express their view on the potential advantages and disadvantages on implementing a standard method for Mn exposure measurements amongst IMnI member companies.

The questionnaire was emailed by IMnI to contacts from 16 member companies on 7th August 2008. The IMnI contacts were asked to disseminate the questionnaire to their production sites and to return the completed questionnaire via email to IMnI by the end August 2008. The returned questionnaires were then forwarded to IOM.

During the preliminary review of the returned questionnaires there were a number of instances where the responses were unclear and which required further clarification. IOM identified such instances and in early October 2008 IMnI contacted the relevant companies and requested the additional information to be returned by 10th October 2008.

Responses from all the returned questionnaires were coded and entered into a Microsoft Excel spreadsheet.

4.3 SURVEY RESPONSES

Nine companies participated in the survey, with a total of 28 sites, located in various countries, including Australia, Belgium, France, Gabon, Japan, Korea, Mexico, Norway, South Africa, Spain and USA.

The following sections described the information gathered in the questionnaires. A detailed summary of the number of responses for each question is shown in Appendix 1.

Section 1: ***Background information***

Information from the surveys showed that around two thirds of the workforces were potentially exposed to manganese on-site (Appendix 1, Table 1).

Most of the sites (71.4%) that responded to the questionnaire were producers of manganese metal and metal alloys. Around 14 to 18% of the sites indicated 'mining' and 'chemical production of manganese metal and metal alloys respectively. No questionnaires were received from companies in the industrial sectors 'steel production', 'other metal smelting processes', 'battery manufacture', 'agricultural products (production and use)', or 'pigments, paints and glass making'. (Appendix 1, Table 2).

Section 2: ***Manganese in workplace air sampling and analytical methods***

The 'total' and 'respirable' aerosol fractions have been the most commonly fractions assessed, both currently and within the past 5 years, although measurement of the 'inhalable' fraction is also frequent (Appendix 1, Table 3). It was also clear from the returned questionnaires that sites commonly carried out sampling for more than one aerosol fraction, usually either inhalable and respirable or total and respirable.

Sites reported to use a variety of sampling heads for assessing the respirable, inhalable and 'total' aerosol fractions, although the 37 mm cassettes, IOM sampling heads and cyclones were found to be reported most frequently. Two companies reported to use a cyclone sampling head for assessing the inhalable fraction (Appendix 1, Table 4). Two companies reported to use PUF as size-selective mediums (IOM inhalable sampler with foam and the CIP samplers).

Regarding the sampling medium used to collect Mn, CE filters were the most preferred sampling medium, being used in 12 of the 28 sites, followed by Polyvinyl chloride (PVC) filters (Appendix 1, Table 5).

Most of the sites (21 out of 28) analysed the samples collected for total Mn, both currently and during the previous 5 year period of the questionnaire being administered. None of the sites reported to analyse other Mn fractions (e.g. water soluble or water insoluble Mn).

Table 5 provides a summary of the samplers used by the sites for sampling of 'total', inhalable and respirable dust, along with details of the sampler's common advantages and disadvantages indicated in the peer-reviewed literature (section 3). The sampling methods most commonly reported were the 37 mm cassettes, IOM sampling head for the 'total' and inhalable fraction and cyclones for the respirable fraction.

The most common analytical methods currently used included Inductively Coupled Plasma – atomic emission spectroscopy (ICP-AES), atomic absorption spectroscopy (AAS) and gravimetric analysis. None of the sites indicated ever using x-ray fluorescence (XRF), neutron activation or colorimetric analytical methods (Appendix 1, Table 6).

A variety of sampling and analytical methods were indicated as being used, with the most commonly reported method used, both currently and within the previous 5 years, the 'NIOSH method 7300 (NIOSH, 2003a) (digestion with nitric/perchloric acid and analysis by ICP). In several instances other methods not included as options in the questionnaire were indicated. These included Australian methods AS2985 (AS, 2004a) and 3640 (AS, 2004b), KOSHA Method-1 and methods used in Mexico (Appendix 1, Table 7).

Table 5 Summary of air sampling methods reported in questionnaire survey for sampling Mn in air

Aerosol fraction	Sampler name	Countries reporting to use sampling head	Disadvantages	Advantages
Total dust	37-mm cassette (both open and closed) / Millipore cassette	USA, Mexico, South Africa, Spain, Norway	Particle deposits on walls[1,2,] Underestimation of particles in the size range from 30-100 µm. [3,6,14]	Recommended method by: NIOSH 0500 (NIOSH, 1994a) OSHA ID 125G (OSHA, 1991) OSHA ID121 (OSHA, 2002)
	25mm cassette			
Inhalable	CIP 10-I CIP T	France	Under-sample the IOM sampler [4,6, 7]	Performance independent of wind speed for particles below 75 µm[3]
	IOM	Australia, Belgium, South Africa,	Over-sample for large particle sizes[6,13,]	Meets ISO/CEN/ACGHI criteria [12] Recommended by HSE, 2000 Performance independent of wind speed for particles below 75 µm[3]
	Multi-orifice sampler (seven-hole) (Casella)	Australia	Performance dependant on wind speed. [3] Under –sample the Inhalable fraction[3,13]	Recommended by HSE, 2000
Respirable	CIP 10-R	France		Meets ISO/CEN/ACGHI criteria[12]
	Casella vortex pump	Norway	It does not sample the respirable fraction. Designed for TSP, PM_{10} and $PM_{2.5}$ [8]	
	SKC Al cyclone	Australia	Biases of 10-30 % for dust clouds for particles > 10 µm [10] Performance dependant on flow rate variability[11]	Meets ISO/CEN/ACGHI criteria[12]
	SIMPEDS cyclone	Australia		
	Cyclone (general)	Belgium, Norway, Spain, USA		
Multi-fraction	IOM foam sampler	South Africa	Under-sample the Inhalable fraction at high dust concentrations[10]	Meets ISO/CEN/ACGHI criteria[12] Dual fraction collection for Inhalable and respirable

[1] Vincent et al. 1995; [2] Demange et al. 1990; [3] Kenny et al. 1997: [4] Kenny et al. 1999; [5] Aizenberg et al. 2000, [6] Aizenberg et al. 2001, [7] Barthley et al.1994; [7] Thorpe et al. 2007; [8] Casella CEL (Belford, UK); [9] Courbon et al. 1978; [10] Harper et al. 1998; [11] Görner et al. 2001; [10] Linnainmaa et al. 2008; [12] HSE, 2000; [13]De Vocht et al. (2006);[14] Teikari et al. 2003

The selection of the sampling and analytical method was governed by the requirements of national regulations and guidance and contracted occupational hygienists. The responses suggest that factors including cost, greater sensitivity, and historical use do not play a major role in determining the use of sampling and analytical methods. The responses from the sites would suggest that companies will use whatever method is required and recognised by the national authorities, and hence likely to be recommended by the occupational hygienist contractors, and this should be considered when proposing a standardised method (Appendix 1, Table 8).

In the questionnaire survey, sites were asked to indicate whether they carried out Mn aerosol sampling and analysis to any recognised standard methods. Table 6 summarises the actual recognised methods reportedly used, along with details of the sampler, collection medium, extraction and analysis method specified within these standards.

Table 6 Standardised methods for the determination of airborne particulate matter and Mn in workplace atmospheres

Standard	Particle size	Sampler	Collection medium	Mn extraction	Analysis method
0500 Particulates not otherwise regulated, total (NIOSH, 1994a)	Total dust	37-mm cassette	PVC	-	-
OSHA ID 125G Metal and metalloid particulates in workplace atmospheres (ICP analysis) (OSHA, 1991)	Total dust	37-mm 3 piece cassette	MCE/PVC	Hot plate HNO_3-H_2SO_4-HCL	ICP-AES
OSHA ID 121 Metals and metalloid particulates in workplace atmospheres (atomic absorption) (OSHA, 2002)	Total dust	37-mm 3 piece cassette	MCE	Hot plate HNO_3-H_2SO_4-HCL	ICP-AES
MDHS 14/3 General methods for sampling and gravimetric analysis of respirable and inhalable dust (HSE, 2000)	Inhalable	IOM	PVC	-	-
MDHS 91 Metals and metalloids in workplace air by x-ray fluorescence spectrometry (HSE, 1998)	Inhalable	as described in MDHS 14/3	MCE	-	XRF
MHDS 99 Metals in air by ICP-AES (HSE, 2006)	Inhalable	as described in MDHS 14/3	MCE	Hot plate HNO_3-H_2SO_4-HCL	ICP-AES
ISO 15202 (ISO, 2004)	Inhalable	as described in EN 13205	Not specified	Microwave assisted	ICP-AES
NIOSH 0600 Particulates not otherwise regulated, respirable (NIOSH, 1998)	Respirable	Higgins Dewell cyclone (2.2l/min) or Aluminium cyclone	PVC	-	-
NIOSH 7300 Elements by ICP (NIOSH, 2003a)	Respirable	Not specified	MCE or PVC	Hot plate HNO_3-H_2SO_4-HCL	ICP-AES
ISO 15202 (ISO, 2004)	Respirable	As described in EN 13205	Not specified	Microwave assisted	ICP-AES
French Norm NF X 43-275 (FN, 2002)*					AA
NOM-010-STPS-1999 (NOM, 1999)*					
MPL WILAB 4 with AS 2985 (AS, 2004a)*	Respirable				
MPL WILAB 6,8 and 17 in accordance with AS 3640 (AS, 2004b)*	Inhalable				
KOSHA Method -1(no reference available)*					
UNE 81587 (UNE, 1994)*					AAS

Note: PVC – polyvinylchloride; MCE-Mixed cellulose ester; ICP-Inductively Coupled Plasma; AA – Atomic Absorption; AAS - Atomic Absorption Spectrometry; AES-Atomic Emission spectrometry; XRF-X-ray fluorescence * unable to obtain reference

There are no standard NIOSH or OSHA methods for sampling personal inhalable dust; instead NIOSH and OSHA standards usually recommend the use of the 37-mm sampling cassette for sampling of ‘total’ dust. The only NIOSH method that describes the use of an inhalable sampler is NIOSH 5700 (NIOSH, 1994b) for formaldehyde on dust, which specifies the IOM sampler or equivalent.

On average, sites collected 91 personal samples on an annual basis, with the majority of the measurements being long-term samples. Far fewer static / area samples were collected and for those sites that provided information, on average 6 static samples (geometric mean, GM =3) are collected annually. This suggests that the companies prefer to concentrate their measurement efforts on personal sampling (Appendix 1, Table 9).

The reason cited for sampling was mostly to assess compliance with OELs and to assess the risk to health. Just under half of the sites also indicated that they carried out measurements to assess the performance of control measures in place (Appendix 1, Table 10).

Most sites employed more than one type of sampling strategy although representative sampling was the most common; with task specific also being very frequent (Appendix 1, Table 11).

Section 4: ***Manganese exposure information collected***

Regarding what contextual information is recorded during the manganese surveys, seven of the 16 contextual items listed were ‘always’ recorded by more than 70% of the sites (Appendix 1, Table 12). These included unique ID number; date of sampling; workers name identify, job title, sample duration, specific location of work and the environment of where the sample was collected.

Data items which were less frequently recorded included size of workroom (never recorded by 17 of the sites); type of general ventilation in operation (never recorded by 8 sites) and exposure pattern (never recorded by 7 sites).

Most of the sites store exposure measurements in reports, these being either electronic or hard copy. Three sites stated that a computer database system such as Access or corporate health surveillance system was used to store their exposure measurements whilst just under half of the sites currently used a spreadsheet such as Excel to store the data (Appendix 1, Table 13).

Section 5: A standardised method for measuring Mn exposure

Most of the sites (24 out of 28) indicated there was a need in the industry for a standardised method for assessing manganese exposure.

When asked about the advantages, if any, there would be to their company in adopting a standardised method the responses suggest that sites feel that a standardised method would provide them with greater confidence and security in any comparisons being made between data collected from different sites and companies as the measurements would be more uniform. Some respondents also indicated that they felt that a standardised method may also lead to the possible adoption of internationally accepted exposure standards and industry standards. They also felt that adopting a standardised method would result in more meaningful benchmarking exercises being undertaken.

Sites were also asked to indicate what they thought the ‘barriers’ or problems their company may have to adopting a standardised method. This question was poorly answer: only 8 sites responded there were no barriers to adopting a standardised method, whereas one site stated that the question was not applicable to them given that they already use a standardised method. The free text responses are shown in Appendix 1, section 5.

A number of other issues were raised, with perhaps the main one being that the standard method must be approved by relevant regulatory the actual authorities. The methods should not be cost prohibitive, should be user friendly (both from the perspective of the occupational hygienist and the wearer). It was also considered that there may be issues regarding capability of laboratories to deal with such samples, that items may need to be purchased and personnel may require training.

Sites were also asked to rank in order of priority those factors which were thought may encourage them to adopt a standardised method. The means of responding to this question was poorly understood by the majority of sites. For example, whilst some responded correctly, others ranked items on a scale of 1 to 3, possibly ranking several items with the same numerical value. One questionnaire contained no responses to this question.

Given the variability in how the statements were answered it is difficult to give a very clear overview of those factors which are felt to be the highest priority with respect to encouraging companies to adopt a new method. Although subject to interpretation, the factors ‘is validated’ and ‘has a greater analytical sensitivity / reliability than existing methods’ were ranked 1 in the most instances. The method being readily available, associated costs being lower than existing method and allowing comparison of results with other sites/ companies were those factors which were perhaps ranked less highly. A summary of the ranking for each statement is provided in Table 14 in Appendix 1.

5 CHEMICAL ANALYISIS OF MANGANESE IN AIRBORNE SAMPLES

5.1 ANALYTICAL METHODS

There are several validated methods that have been developed for analysis of Mn in air samples collected on filter to support the implementation of existing regulatory exposure standards. Most methods use either ICP-AES or AAS. ICP-MS is a relatively expensive technique. Sample preparation involves heating the collected dust and filter in concentrated acid, followed by dilution (Table 7).

Table 7 Sample preparation methods for analysis by ICP or AA (conc: concentrated)

Method	Digestion	Analysis Solution
OSHA ID 121 total metal (OSHA, 2002)	Heat in conc. HNO_3; reduce to dryness; add further HNO_3; reduce to 1 ml	Make up to volume with distilled water (=4% HNO_3)
OSHA ID 121 soluble metal* (OSHA, 2002)	Extract in deionised water	
OSHA ID 125-G (OSHA, 1991)	Add 1:1 H_2SO_4, followed by conc. HNO_3; leave for 1 hour; add several drops of 30% H_2O_2; heat cautiously till brown; add drops of H_2O_2 to clear solution; heat until fumes of SO_3 appear; cool; add conc. HCl heat until near boiling	Make up to volume with deionised water
NIOSH 7301 (NIOSH, 2003c)	Heat in aqua regia (1HNO_3:3HCl) at 120^{o}C; reduce to 0.5ml; add further aqua regia and repeat till solution clears; reduce to dryness	Make up to volume with 5% aqua regia
NIOSH 7303 (NIOSH, 2003d)	Add 1.25 ml conc. HCl; place in hot block and heat at 95^{o}C for 15 minutes; cool; add 1.25 conc. HNO_3, heat in hot block for a further 15 minutes	Make up to volume with distilled water

*For metals with exposure limits for the soluble form of the metal – not Mn

The detection limits quoted by these methods vary (Table 8). However, in practice the detection limit achieved in an individual laboratory will depend to a large extent on care taken in sample preparation. All methods described in Table 7 have been demonstrated to give good recovery of Mn from spiked samples representative of Mn compounds in workplace air (Table 8).

Table 8 Detection limits and recovery efficiencies quoted for Mn

Method	**Detection Limit µg filter***		**Sensitivity µg/filter***	**Variation Coefficient (%)**	**Average recovery (%)**
	Qualitative	**Quantitative**			
OSHA ID 121 AA	0.05	0.25	1.375	4.4	100.2
OSHA ID 125G ICP	1.525	5	14.1%	3.2	95.2-98.7
NIOSH 7301 ICP	-	0.005	-	-	103.5 %RSD 1.64 (0.31 µg on filter) 91.2 %RSD 2.01 (1.29 µg on filter)
NIOSH 7303 ICP	-	0.1	-	-	-

*25 ml final sample volume; AA-Atomic Absorption; ICP-Ionization Coupled Plasma; RSD-Relative Standard Deviation

There is less information about the validity of these methods in complex mixtures where other elements in the sample may cause interferences with the analysis. Interferences may arise from:

- Chemical reactions in the flame (AA).
- Poor matrix matching of calibration standards and sample solutions (AA or ICP).
- Ionization of the element of interest in the flame changing the absorption spectrum of the analyte, effectively removing atoms from the flame (AA).
- Spectral interferences where an element other than the one analyzed absorbs (AA) or emits (ICP-AES) at the same wavelength giving rise to an over-estimate of the quantity of the analyte that is present.
- Background absorption interferences (AA) including flame absorption, molecular absorption, and light scattering.
- Large quantities of silicate or other particulate material that can interfere with sample delivery.

With both AA and ICP, spectral interferences may be avoided by using an alternative wavelength for analysis and problems caused by suspended particulates in analysis solutions can be eliminated by filtering samples prior to analysis.

Possible interferences with Mn in analysis by AA include phosphate, perchlorate, iron (Fe), niquel (Ni), copper (Cu), wolframium (W), molybdenum (Mo) and silicon (Si). Chemical interferences when using AA can be controlled by using a hotter flame, or by the addition of a releasing agent which inhibits the reaction between the metal and the interfering species. Ionisation interference can be controlled by adding an easily ionized metal such as Na, K, Cs, or rubidium (Rb). Flame absorption can be controlled by a variety of mechanisms including optimization of fuel and oxidant flow rates, use of flames which are more transparent at these wavelengths (i.e., Air/H_2 or argon/hydrogen flames), or deuterium arc background correction (DABC). Molecular absorption is controlled by using hotter flames to break down molecular species or by DABC. During analysis by ICP, the high temperature of the plasma minimizes most chemical and matrix interferences.

Ellingsen et al. (2002) collected samples of welding fume for Mn analysis on PVC filters. Samples were placed in a Teflon autoclave and 2ml of aqua regia and 0.2 ml hydrofluoric acid added. A known quantity of beryllium chloride was added as an internal standard. The autoclaves were heated in a microwave unit. The digests were then diluted to 15 ml prior to analysis by ICP-optical emission spectrometric measurement using reference standards prepared in house for quality control that were traceable to international certified materials. The accuracy and reproducibility (day to day variation) was claimed to be ≤ 2% or better.

As an alternative to acid digesting airborne metal samples and analysis by ICP or AA, it is possible to analyse for metals directly on filter using X-ray fluorescence spectroscopy (MDHS 81, HSE 1998). The advantage of direct on filter methods is that the potential for sample losses during preparation prior to analysis is greatly reduced. It is particularly useful for the analysis of welding fume on filter. The disadvantages are that particle size and the thickness of the deposit on filter can affect the results of XRF analysis. The MDHS states that provided that the average particle size is less than 2.5 µm and less than 0.5 mg of sample has been collected, the negative bias caused by particle size effects will normally be below 10%.

The detection limit for Mn on filter by XRF is 0.4 µg (qualitative) and 1 µg (quantitative). Lower detection limits can be obtained by counting for longer periods. For Mn the maximum overall uncertainty for samples that are between 0.5 and 2.5 $mg.m^{-3}$ in a 60 litre sample (minimum recommended by MDHS) would be 25.3% reducing to 25.1% for samples that are 2.5-10 $mg.m^{-3}$.

Thomassen et al. (2001) developed a four step digestion method for samples collected on cellulose ester membrane filters to determine the relative proportions of different Mn species in workplace air in a Mn alloy producing plant that was also used by Ellingson et al. (2000). The four components were:

1) “Water soluble” Mn (ion exchangeable compounds).
2) Mn metal, FeMn alloys, MnO and Mn^{2+} part of Mn_3O_4.
3) The nondissolved Mn^{3+} part of Mn_3O_4, Mn_2O_3 and MnO_2.
4) Mn in silicate minerals or as insoluble SiMn alloy that is not likely to be bioavailable.

The optimised leaching conditions are shown in Table 9. Ammonium acetate was selected as a suitable solvent on the basis of its use in soil leaching studies undertaken to establish the bioavailable metal fraction. Table 10 shows the experimentally determined efficiency of the four step digestion procedure as determined from experiments involving known mixtures of pure phases.

Table 9 Optimised leaching conditions developed for investigating Mn speciation

Step	Component	Reagent	Conditions
1	Water soluble Mn	0.01 M ammonium acetate	90 minutes 20°C
2	Mn^0 and Mn^{2+}	25% acetic acid	90 minutes 75°C microwave-assisted heating
3	Mn^{3+}, Mn^{4+}	0.5% hydroxylamine hydrochloride in 25% acetic acid	90 minutes 75°C microwave-assisted heating
4	Insoluble Mn	Aqua regia: hydrofluoric acid 4:1	Closed Teflon autoclaves, Microwave-assisted heating

Table 10 Leaching recovery (%) of pure Mn compounds with well defined stoichiometries

Compound	Component 1 Water soluble	Component 2 Mn^0, Mn^{2+}	Component 3 Mn^{3+}, Mn^{4+}	Component 4 Insoluble
MnO	<1	96±1	<1	<1
Mn_2O_3	<1	<1	94±3	<1
Mn_3O_4	<1	100±8	97±2	<1
MnO_2	<1	<1	95±1	<1
Mn	3±0.3	90±3	6±1	<1
FeMn	<1	100±1	<1	<1
SiMn	<1	<1	<1	98±2
Quality control mixture	<1	90±6	92±2	97±2

5.2 QUALITY ISSUES

Analytical laboratories should ideally be accredited to ISO 17025 (for metals analysis) (ISO, 2005). This ensures the use of traceable analytical standards, calibrated glassware, analytical grade acids, internal method validation and determination of detection limits and re-analysis of an appropriate number of replicate samples. It also ensures that staff are properly trained and participate in ongoing performance checks such as internal sample exchanges in which all analysts in the laboratory analyse a single set of samples.

Inter-laboratory variability is inherent in any kind of analysis. Even where analyses are performed using apparently identical protocols, results from different laboratories normally differ slightly. Therefore, laboratories should participate in an external proficiency testing scheme for metals analysis on filter. Examples of such proficiency schemes include:

- WASP - the UK Workplace Analysis Scheme for Proficiency. WASP circulates sets of 4 samples quarterly for a range of metals including Mn.
- IHPAT, Industrial Hygiene Proficiency Analytical Testing, a testing scheme sponsored by the American Industrial Hygiene Association. IHPAT circulates samples for metals analysis but Mn was not on list of analytes during recent rounds.
- German BGIA - Institutions for Statutory Accident Insurance and Prevention, Institute for Occupational Safety. The BGIA round-robin tests for metals provide participants with about 1 g of a dust for analysis in order to identify five metals, e. g. Ni, Pb, Co, Cu and arsenic (As).

The German round robin scheme did include Mn in 2007, but not in 2008. The analysis of most metals employs similar methods such that competency in the measurement of one metal is likely to indicate competency across a broad range of metals. However, if a laboratory specifically wished to prove ongoing competency in the analysis of Mn, it would clearly be desirable to participate in WASP for Mn.

Mn in workplace air is a relatively easy analysis compared with some occupational hygiene analyses and the anticipated uncertainty around reported results would be ≤10%, consistent with the level of precision achieved for other metals that are routinely measured in workplace air. Laboratories who have participated in a recent round of WASP for Mn, for example, were able to achieve results that were within 10% of the mean value (Figure 7) with a similar spread of results being observed for iron, copper, chromium, zinc, cadmium, lead, nickel and cobalt (Figure 7). A similar level of variability was reported in a past BGIA round robin for the analysis of the proportion of different metals in a sample of dust (Table 11).

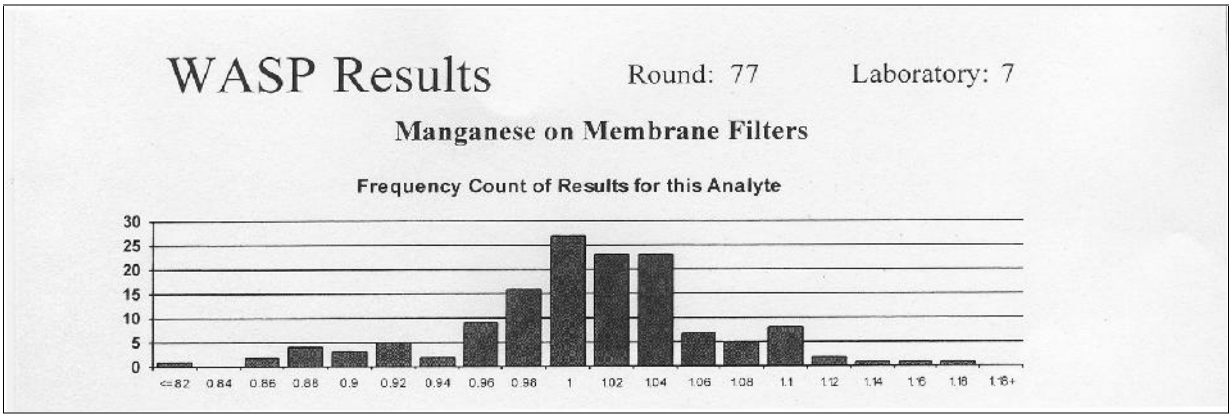

Figure 7 Performance of participants in WASP for Mn

Table 11 Comparison of precision of analysis for Lead (Pb), Iron (Fe), Cobalt (Co), Manganese (Mn) and Nickel (Ni) in dust in the BGIA round robin

	Pb	Fe	Co	Mn	Ni
Relative standard deviation %	6.46	8.88	5.31	8.49	5.33

5.3 CONCLUSIONS

There are well established analytical methods to support the routine monitoring of workplace air for Mn to meet current regulatory exposure standards. Both AA and ICP-AES are equally suitable and can both be used. Methods are also available to enable the speciation of airborne Mn into up to 4 fractions of differing solubility. While useful as a research tool, the additional sample preparation and analysis costs would be substantial in comparison to the costs of the traditional method of analysis for total Mn.

It is important that any implementation of a standard or reference method for measuring Mn in air amongst member companies of IMnI, is supported by a quality control scheme, for example by joining existing proficiency schemes such as WASP.

6 PROPOSAL OF A STANDARD SAMPLING METHOD FOR MEASURING MN

Based on the information from the literature review, together with information collected through the questionnaires, IOM proposed five candidate methods for measuring Mn in air. These being:

1) Higgins-Dewell cyclone (respirable dust).
2) IOM Inhalable dust sampling head.
3) CIP 10 R (Respirable dust).
4) CIP10 I (Inhalable dust).
5) IOM dual fraction sampler (inhalable and respirable fraction).

These five methods were based, in the first instance, on the following criteria:

- The recommended sampler(s) should meet the sampling criteria for measuring the inhalable and/or respirable dust as defined by CEN/ISO/ACGIH.
- The choice of sampling head and medium should not impede any subsequent chemical analysis for manganese or manganese compounds.

In addition, results of the questionnaire to IMnI member companies identified the following factors that needed to be considered when selecting a standard sampling method:

- Validity, reliability, sensitivity.
- Ease of use.
- Burden on the wearer.
- Costs of sampling and analysis.
- Availability of sampling head.
- Sampling equipment should not impede on any safe working practices.
- National regulatory requirements.
- Available technical capabilities for chemical analyses.

Also, it would be a great advantage if the method is able to sample for both health-related dust fractions (inhalable and respirable dust) simultaneously, since this would reduce the burden on the wearer.

These methods were presented to the IMnI company’s representatives in a teleconference in December 2008. Copies of the discussion documents circulated at the teleconference concerning this are provided in Appendix 2.

Further to the discussions which took place during the teleconference two points emerged which impacted on the choice of sampling methods:

1. The foam component of the IOM dual sampler was withdrawn from circulation and was not expected to be available during the proposed time period of the sampling surveys. This sampler was therefore excluded from the comparisons. An alternative to the IOM dual sampler was identified, this being the CIS Inhalable sampler (BGI Inc.) which also allows both the inhalable and respirable fractions to be measured simultaneously. Based on the literature review, the CIS was considered, an acceptable alternative candidate method that should be included in the study.

2. The proposed CIP 10 samplers represented a significant capital outlay and measures to reduce these capital costs, for example hiring or borrowing the samplers, were unsuccessful. Following much further discussion the decision was taken to remove the CIP sampler from the candidate methods.

Following further review and discussion, the following candidate methods for sampling Mn in the inhalable and respirable dust fractions were selected to be compared:

Inhalable dust fraction	Respirable dust fraction
IOM inhalable dust sampler	Higgins-Dewell cyclone
Conical inhalable dual fraction sampler	Conical inhalable dual fraction sampler

Details of the three selected samplers are provided in sections 3.2.3 and 3.2.4. A summary of the approximate costs from one supplier (Casella Measurements) is shown in Table 12, with a further list of suppliers being provided in Appendix 3.

Table 12 Cost (£) of the three proposed sampling devices and sampling mediums (cost at June 2010. Supplier: Casella measurements). For a list of suppliers see Appendix 3.

	IOM head	HD cyclone	CIS
Sampler body	43	42	50
Sampling cassettes	7	5	13
Sampling medium	23 25-mm GF/A filters (pack of 100)	30 37-mm GF/A filters (pack of 100)	130 PUF (pack of 100) 30 37-mm GF/A filters (pack of 100)
Total cost for 5 samples collected simultaneously	256	343	355

PUF:Polyurethane foam; GF:Glassfibber

The CIS sampler is the most cost effective method as both dust fractions are collected simultaneously. The chemical analysis of each sampling medium has a similar cost. It should be borne in mind that the use of the CIS sampler involved analysis of two sampling mediums.

It was also intended that any inhalable or respirable sampler already being used by a site participating in the sampling surveys would also be compared during the field campaign.

It was intended that four field sampling surveys would take place at Mn producer companies to assess the samplers, with each survey taking place over a 5-day period. Since the principal objective of the field exercise was to compare samplers rather than to estimate exposures, the main criteria for selection of sampling areas and employees was that they would provide a spectrum of potential Mn exposures, a range of different industrial processes and that the management and workforce were supportive to the study, with personnel being familiar with the wearing of sampling equipment

A combination of side-by-side personal and static, area, and measurements was planned in order to compare the samplers. At each site, the aim was to collect both personal and static exposure measurements, from a variety of jobs and locations. The exact number of measurements to be collected was to be determined following the preliminary site visit and specified in the company specific sampling strategy. It was intended that the samplers would be compared for a range of concentrations, with comparisons being carried out on the basis of mass and total Mn.

7 FIELD EVALUATION OF THE PROPOSED STANDARD METHODS FOR COLLECTION OF DUST AND MN

7.1 INTRODUCTION

The three selected sampling devices: the IOM inhalable head, the CIS and the HD cyclone were compared on four Mn production sites. To test the samplers, side-by-side personal (IOM vs. CIS and cyclone vs. CIS) and static measurements (IOM vs. CIS vs. cyclone) were performed at each of the production sites. Since the principal objective of the field exercise was to compare samplers rather than to estimate exposures, the main criteria for selection of sampling areas and employees was that they would provide a spectrum of potential Mn exposures, a range of different industrial processes and that the management and the workforce were supportive to the study, with personnel being familiar with the wearing of sampling equipment

Samplers were compared on the basis of dust mass and total Mn.

7.2 METHODS

Introduction
A protocol was developed for the study to ensure a systematic approach on the execution of the sampling campaigns (Appendix 4). This protocol provides details of how the preliminary work was undertaken: how companies were recruited, development of the sampling strategy, the procedures adopted during the sample collection, analysis of the collected samples and data analysis. In an effort to avoid repetition of information, the following sections highlight the most important factors of each stage. For a complete description of the field work procedure, see Appendix 4.

In the first instance, companies were asked to participate in the study. Those who showed an interest were provided with the details of the monitoring campaign and what it would be expected from the site personnel. For those who agreed to participate in the study a site visit when possible or a phone conference was organised to obtain information on the site (e.g. industrial processes, Mn compounds produced at the site, number of employees, potential exposure levels etc…). Following the preliminary site visit a specific sampling strategy was developed for each site. This was circulated to the site to allow feedback and final confirmation of the work that it would be undertaken.

In addition to the field survey, a small study was undertaken to examine particle losses during transportation from the site to the IOM laboratory.

7.2.1 Company recruitment

The IMnI asked Mn producer companies to volunteer to allow field surveys to take place in one of their production sites. Those companies who expressed an interest in participating in the study were contacted by the IOM, initially via email and then follow-up teleconference call to provide further information on the aims and objectives of the study and to identify suitable sites to participate in the field survey.

For those company sites who agreed to participate in the study, a preliminary site visit, where possible, was arranged to obtain the necessary information to develop a site specific sampling strategy (section 7.2.3) for use in the field survey. In instances where a preliminary site visit was not possible, a series of telephone conferences took place to obtain the necessary information. The site specific sampling strategies were circulated to the company in-site personnel prior to the field survey to obtain feedback and agreement from the site on the work that it would be undertaken.

7.2.2 Sampling strategy

The sampling strategy included information on the:

1. Description of the industrial processes at the site.
2. Manganese compounds being produced at the site.
3. Times of production shifts and number of employees working per shift.
4. Potential areas/personnel exposed.
5. Company sampling methods.
6. Anticipated work programme on site.

The sampling strategy aimed to collect 10 sets of area measurements (IOM vs.CIS vs. cyclone) at each site and 20 sets of personal measurements (10 CIS vs. IOM & 10 CIS vs. cyclone) at each site. This would result in a total of 80 pairs of area and 80 pairs of personal measurements (40 CIS vs. IOM & 40 CIS vs. cyclone, Table 13).

Table 13 Number of paired samples aimed to collect for the study

Measurements	Number of sets per site	Total number of sample pairs collected at the 4 sites
Area CIS vs. IOM vs. cyclone	10	40 CIS vs. IOM 40 CIS vs. cyclone
Personal		
CIS vs. IOM	10	40 CIS vs. IOM
CIS vs. cyclone	10	40 CIS vs. cyclone

For those sites where other sampling methods were used to measure exposure to Mn it was intended to compare these on-site methods with the candidate methods. However, all companies but one used the same sampling methods proposed: the IOM head for the inhalable fraction and the cyclone for the respirable fraction. One company used the 37-mm close cassette for the total/inhalable fraction a 37-mm close cassette with a cyclone to collect the respirable fraction (this method collects the fraction of particles with a diameter less than 4 µm with a 50% efficiency). In this case, static samples were co-located with the company samples, i.e. (IOM vs. CIS vs. cyclone vs. 37-mm cassette & 37-mm cassette + cyclone). Results have not been presented in this report at the company's request. The unique measurement method used would reveal the company's identity.

The sampling strategy was circulated to the relevant site personnel prior to the sampling survey to obtain feedback and agreement from the site. The sampling strategy was revised as necessary during the sampling campaign to accommodate reactive changes to Mn production.

7.2.3 General sampling procedure

Mn exposure measurements were carried out over a 4 or 5-day period. Sampling duration was intended to be at least 5 hours.

The cyclone and the IOM head were loaded with a 34-mmn and 25-mm fibre glass filters (GF/A), respectively (Casella, Belford, UK.). The CIS sampler was loaded with a PUF (a large black foam with a smaller white foam at the bottom and a 37-mm fibre glass filter to collect respirable particles (both from Casella, Belford, UK.). All sampling media were conditioned and weighed before and after sampling at the IOM laboratory in Edinburgh.

Samplers were attached to an APEX personal sampling pump (Casella, Belford, UK) or SKC personal sampling pump (Model AirCheck 52, SKC Ltd. Dorset, UK). SKC pumps were used only for area sampling with the IOM head and cyclone as they are heavier and noisier than the APEX pumps. SKC pumps are not suitable for use with the CIS sampler as their flow rate only reaches 3.0 $\mathrm{l.min^{-1}}$, whereas the CIS sampler requires 3.5 $\mathrm{l.min^{-1}}$.

All flow rates were measured (± 0.01 $\mathrm{l.min^{-1}}$) twice at the beginning and end of the sampling period using a calibrated digital flow meter. Samples for which the Relative Standard Deviation (RSD=SD/ AM*100) of the flow rate was larger than 10% of the set value were removed from the dataset. The samplers were connected to sampling pumps by Tygon® tubes.

For personal samples, the two pumps were secured to the operator by attaching to a belt worn around the waist. Both sampling heads (CIS & IOM or CIS & cyclone) were clipped to the same side of the lapel of the overalls (dominant side of operator), within the breathing zone, i.e. within 200 mm of the nose and mouth. The position of the samplers in relation to the operator's lapel was alternated from operator to operator. Once the pumps and sampling heads were attached satisfactorily, the pump was switched on and the time recorded. The aim of the sampling exercise and the importance of wearing the samplers at all times were explained to the operators. At the end of the sampling period, the flow-rate was checked and recorded, the pump was switched off and the time noted.

For the static measurements the three samplers were located in fixed points at breathing zone height. The relative position of the samplers was alternated.

For each sample, details on sampling duration, sample and pump code, area sampled, or task/activities carried out during sampling and the relative position of the samplers were recorded. Employees were asked to fill out a questionnaire giving details of their job/tasks during the duration of the sampling (Appendix 5). This questionnaire was translated as necessary for the site operators.

Field blanks (filters and foams loaded into the cassettes and taken to the field but never exposed to the workplace air) were collected at the four Mn production facilities.

7.2.4 Assessment of sample losses during transport

To examine whether dust particles were dislodged from the sampling medium during transportation from the Mn manufacturing site to the IOM laboratory in Edinburgh, a small additional study was undertaken. Four sets of one IOM sample, one cyclone, and one CIS sample were weighed at two of the sites (2 sets at each site) following sample collection, and the weight was compared with the weight at the IOM laboratory. Three blanks for each sampling medium were weighed along the samples and the difference in weights was used to adjust the samples weights. Samples and blanks were conditioned in the weighing room for 24 hours prior to weighing. The balance was calibrated according to the manufacturer instructions.

This small study aimed to give an overview on potential losses during transportation but it was not intended to be a comprehensive evaluation. A much larger study, involving a larger number of samples would need to be undertaken to determine the significance of the results obtained in this small survey.

7.2.5 Gravimetric analysis and Chemical analysis

Gravimetric analysis was performed using a modification of the MDHS 14/3 method (HSE, 2000). All sampling mediums (including the IOM cassettes) were conditioned for 24 hours in a temperature and relative humidity controlled room prior to weighing. A series of controls (fitters and foams) were weighed with the un-exposed and exposed sampling mediums and the difference in weight was used to correct the samples. Laboratory blanks (filters and foams from the same package as the exposed sampling medium but never taken outside the laboratory) were also weighed along with the un-exposed and exposed sampling medium.

The LOD of the gravimetric method was 0.05 mg per filter and 0.1 mg per foam. Therefore the LOD of the inhalable and respirable fractions of dust collected with the CIS sampler were 0.1 and 0.05 mg. Dust concentrations in the filter have been expressed in mg.m^{-3}.

Filters used with the cyclone and CIS sampler as well as the foams used with the CIS samplers were weighed without the cassettes. Filters used with the IOM samplers were weighed with the cassettes as it is been shown that some particles are stick to the wall of the cassettes.

After gravimetric analyses, the samples were prepared for analysis of their total Mn content using a modification of OSHA ID121 (OSHA, 2002) and analysed by ICP/AES. The LOD of the analytical method is 0.1 µg per sample. Mn concentrations in the filter have been expressed in µg.m^{-3}.

7.2.6 Data analysis

All sample results were field blank corrected, i.e. the mean of the concentration found in the field blanks was subtracted from the concentration found in the exposed sampling mediums. The inhalable concentration for the CIS sampler was calculated as the sum of the mass found in the filter (respirable fraction) and the mass found in the foam divided by the corresponding flow rate.

Differences in concentration between samplers were examined using the ratio of the concentration (CIS-Inhalable: IOM and CIS-Respirable: HD cyclone). Data was log-normally distributed; therefore AM, GM, geometric standard deviation (GSD), maximum (max) and minimums (min) are presented to describe the central tendency of the concentrations. To examine whether the differences in the concentrations were random or systematic the least square regression equation and coefficient (R^2) on the log-transformed data were calculated. The IOM was designated as the independent variable as this sampler has been considered to be more accurate in previous studies (Mark and Vincent, 1986; Kenny et al. 1996 and Lidén et al. 2000).

Data were also analysed to examine whether the differences in the concentrations between samplers were significant after taking into account effects of site and process (presence of dust, or presence of dust and fume). A list of the processes classified as ‘presence of dust’ or ‘presence of dust and fume’ is shown in Appendix 6.

Because of the different factors affecting personal and static samples, summary statistics of the exposure data were analysed separately for both sample types.

7.3 WORK PLACE DESCRIPTIONS

A total of four Mn producer companies agreed to participate in the sampling campaigns. The following section describes briefly the workplace and working practices for the four production sites included in this survey.

7.3.1 Site one

The site manufactures manganese carbonate (Mn_3CO_3), sulphate ($MnSO_4$) and manganese oxides (MnO_4). The site consisted of two main production areas (one for Mn_3O_4 and another one for MnO production) and two packing areas (one for Mn_3O_4 and $MnSO_4$ another one for $MnCO_3$).

The Mn ore is 'wet milled' to produce a 'slurry'. The slurry is mixed with the nitric acid to produce a Mn nitrate ($Mn(NO_3)_2$ solution. The $Mn(NO_3)_2$ solution is then used to produce MnO_3 / MnO_4 powder which is then packed at the main site. $MnSO_4$ production involved reaction of the $MnCO_3$ with sulphuric acid H_2SO_4 and precipitation with NH_3 and CO_2.

Site one reported that they normally use the IOM head and cyclone for collection of the inhalable and respirable fractions respectively.

Personal measurements were carried out for the following jobs:

- Foreman (all production areas).
- Foreman-warehouse.
- Mechanical Maintenance.

Static measurements were carried out in the following areas:

- Mn_3O_4 production.
- MnO packing.
- MnO production.
- Mn_3O_4 packing (end of packing line).
- Staff (resting) room in MnO production area.

7.3.2 Site two

The second site was a ferromanganese producer. The main processes involved siterisation of the Mn ore, reaction in the furnace and crushing of the furnace product.

Personal measurements were carried out for the following jobs:

- Furnace controller.
- Sinter Operator.
- Tapping operator.
- Crushing operator.
- Control Room operator.
- Driver (tapping area).
- Mechanic (all areas).
- Production manager.

Static measurements were carried out in the following areas:

- Control room.
- Sintering.
- Tapping..
- Electrode area.
- Sinterisation.
- Crushing and storage of final product.

7.3.3 Site three

Site three was a producer of electrolytic manganese. The Mn ore is milled in its dry state, calcined at 950ºC and leached in sulphuric acid to convert the solid state Mn into a liquid phase manganese sulphate solution. Impurities are removed in a precipitation process and Mn is then extracted from the purified solution.

After plating, the metal chips are removed from the cathode plates and conveyed to the Materials Handling Section, with the final product manufactured ranging from metal chips to milled powder.

Site three reported that they normally use the IOM head and cyclone for collection of the inhalable and respirable fractions respectively.

Personal measurements were carried out for the following jobs:

- Forklift driver.
- Powder operator.
- Briquette operator.
- Knock off of Mn in electrolytic plate.
- Cell house grader/sampler (take samples from the Mn solution).
- Electrolitic cell maintenance.
- Funkey driver.
- Filtering of the Mn solution.
- Oremill controller.
- Stores supervisor.
- Calciner.

Static measurements were carried out in the following areas:

- Mn_3O_4 production.
- Furnace area.
- Storage of personal protection equipment.
- Redler catwalk, area above calciner.
- Crushing area.
- Topside of cell house.
-

7.3.4 Site four

Site four produces a silicomanganse and ferromanganese alloys. The ore is fed around the electrodes through which electricity is fed, causing the reduction of the ore. The furnaces are tapped; the slag or waste material removed and the molten alloys are cast in layers on top of each other or onto a casting machine. Oxygen is blown into the hot metal while it is stirred with carbon dioxide to reduce the alloys carbon content thereby creating the alloys. The products are crushed and screened to customer specifications.

Site four reported that they normally use the IOM head and cyclone for collection of the inhalable and respirable fractions respectively.

Personal measurements were carried out for the following jobs:

- Crane driver.
- Laboratory.
- Control room operator.
- Pelletizing.
- Crusher.
- Metal tapper.
- Casting bay.
- Tapper.
- Gas plant controller.
- Forklift driver.
- Tippler.
- Crane operator.

Static measurements were carried out in the following areas:

- Tapping.
- Slag crushing & stockpiling area.
- Casting onto floor/skimming.

7.4 RESULTS

Dust and metal concentration in laboratory and field blanks

Results of the dust and metal concentration found in the laboratory blanks and field blanks are shown in Table 14. The CIS and cyclone samplers use the same type of filter and therefore results of the laboratory blanks are shown together. Results from the field blanks are shown separately as the filters were mounted in each corresponding cassettes.

Table 14 Dust and Manganese mass found in the laboratory and field blanks

		Dust (mg)				Mn (µg)			
Sampling	**medium**	**Foam CIS**	**Filter CIS**	**Filter Cyclone**	**Filter IOM**	**Foam CIS**	**Filters CIS**	**Filters Cyclone**	**Filters IOM**
Laboratory Blanks	n	6	13		7	2	6		6
	AM	< 0.1	< 0.05		< 0.05	6.03	< 0.1		0.22
	SD	0.23	0.02		0.02	2.22	0.09		0.19
Field Blanks	n	8	8	9	10	8	8	9	10
	AM	< 0.1	< 0.05	0.07	< 0.05	4.31	1.41	4.73	0.55
	SD	0.08	0.02	0.06	0.01	4.00	0.53	4.11	0.59

The mass of dust in the laboratory and field blanks was below the LOD of the gravimetric method (0.05 mg for filters and 0.1 mg for foams) in all cases except in the field blank for the cyclone, where the mass was only 0.06 mg.

The mass of Mn in the laboratory foams was much higher (6.03 µg per foam) than that found in the filters used with the cyclone and IOM head (<0.1 and 0.22 µg/filter, respectively). The larger variability in the Mn content observed for the foams (SD=2.22 µg per foam) could be partly a result of the lower number of foams analysed (n=2) compared to the number of cyclone and IOM filters analysed (n=6). However, the mass of Mn and the SD found in the field blank foams (n=8) was also much larger than that found in the other sampling mediums, suggesting that the Mn content in the blank foams is higher and more variable than that found in the filters used with the IOM head and the cyclone.

The mass of Mn found in the field blanks was slightly higher compared to that found in the laboratory blanks, suggesting a small degree of contamination in the room where the samplers were loaded.

7.4.1 Issues arising during the field surveys

Several issues were encountered during the sampling campaigns that may have had an impact on the sampler comparison findings.

Despite the operators being given instructions to wear the samplers correctly at all times and to be careful not to cover the sampler's inlet with the jacket's lapel, it was observed that this was not always the case. Some times it was observed the operators took off their jackets and left the samplers behind while they kept working or during breaks. In some instances the tubing connecting the sampler with the pump was bent resulting in the pump switching itself off. In other instances the tubing was pulled out from the pump inlet. Due to security restrictions around some of the work areas and the simultaneous deployment of multiple samplers, it was not possible be certain that samplers were correctly worn at all times during sampling. Therefore, in this study the concentrations measured in personal samples are thought to be less reliable than area samples in terms of measurement precision and accuracy. However, depending on the nature of the workplace, personal samples are still likely to provide a better indication of exposure levels on most occasions.

7.4.2 Usability

The three samplers were considered suitable for occupational hygiene purposes. They were found to be easy to use in terms of loading and unloading the sampling media and cleaning. In addition, all three samplers are light and small minimising inconvenience to the wearer. The advantage of the CIS is that only one sampling pump is needed as the sampler collects both particle fractions, whereas if both fractions are collected with separate samplers two pumps are required. No problems were encountered with the sampling operation (e.g. tendency to block or overload).

The only concern with the samples was regarding the transportation of the foam/filter set for the CIS sampler. The cassettes containing the foam on the top and the filter at the bottom were wrapped in cling film and kept in plastic bags. On arrival to the IOM laboratory it was observed that part of the plastic film had got stuck to the foam and it had to be removed carefully with tweezers. This may have an impact on the results: 1) some of the dust particles deposited on the foam could have been dislodged together with the cling film, leading to an underestimation of the dust and Mn concentrations. Although this is thought to be unlikely as the particles are embedded in the foam; 2) despite IOM staff ensuring that all visible fragments of film were removed, small pieces of the film might have been incompletely removed, leading to overestimation of the dust concentrations. This would not have affected the Mn concentrations.

The main issue identified related to the gravimetric analysis was the higher instability of the foams compared to the filters used by the IOM and cyclone. The LOD is 2 times higher (0.1

mg) than that for the filters (0.05 mg), since the foams are difficult to stabilise to a constant weight. In addition, as explained in section 7.4.1, the Mn mass found in the blank foams was much higher compared to that found in the glass fibre filters used with the cyclones and IOM head. The chemical analysis of the foams did not result in any problem, with the foams dissolving easily in the acid.

7.4.3 Assessment of sample losses during transport

To have an insight in the possible particle losses during transportation, the mass of the sampling mediums (after being exposed) weighed at two of the sites was subtracted from the mass of the sampling mediums weighed at the IOM laboratory. Results are shown in Table 15.

Table 15 Sample losses during transportation (n=4)

	Cyclone	IOM	CIS
AM (mg)	-0.034	0.095	-0.200
SD (mg)	0.001	0.000	0.000

The sampling medium used with the CIS sampler (glass fibber filter plus foams) showed the largest losses in mass with an AM of 0.200 mg lost during transportation. For this study, the foams and filters were weighed together to prevent contamination. Therefore it is not possible to distinguish whether the particle losses were from the filter, foam or both. No losses were observed for the filters in the IOM cassettes: filters gained 0.095 mg, which is close to the LOD of the gravimetric method (0.05 mg). These results indicate that the dust mass (and possibly the Mn mass) collected with the cyclones and CIS has possibly been slightly underestimated. The difference in the mass of the blank sampling mediums was less than 0.000 mg, suggesting that the differences in the weight observed in the exposed sampling mediums were not related to the different environmental conditions (e.g. relative humidity) in both laboratories.

Due to these results being based on a limited number of comparisons, the collected field samples were not corrected for potential sample losses.

7.4.4 Data availability

In the four field surveys a total of 423 measurements were collected. Sixty-four samples had to be discarded due to issues with the sample collection, e.g. pump failure, return of sampling apparatus to researcher with the tube connector off the pump, delivered with the pump switched off or RSD of the flow rate greater than 10%. In total, 332 measurements were suitable for analysis: 172 personal (30 inhalable samples collected with the IOM head, 55 inhalable and 55 respirable collected with the CIS and 32 respirable collected with the cyclone), and 160 static (41 inhalable samples collected with the IOM head, 39 inhalable and 39 respirable collected with the CIS and 41 respirable collected with the cyclone) plus 35 field blank measurements. The number of paired measurements (samples collected simultaneously with the different samplers) is shown in Table 16.

Table 16 Number of inhalable and respirable paired measurements

	Company				
	1	**2**	**3**	**4**	**All**
CIS-I-IOM pairs (inhalable)	15	14	10	15	54
Personal	5	4	5	10	24
Static	10	10	5	5	30
CIS-R-Cyclone pairs (respirable)	15	20	13	10	58
Personal	5	5	8	5	23
Static	10	15	5	5	35

A total of 52 dust samples and 8 Mn samples showed masses below the LOD of the analytical method. These samples were assigned half value of the detection limit (0.025 mg for dust and 0.05 µg for Mn) as is common practice in this type of analysis. Table 17 describes the number of samples below the LOD according to each sampler.

Table 17 Number of measurements below the limit of detection

	Dust		Mn	
	Personal	Static	Personal	Static
CIS (inhalable)	1	7	0	0
CIS (respirable)	8	8	0	2
IOM	1	4	0	0
Cyclone	10	13	3	3

7.4.5 Dust concentrations

Figure 8 shows the probability plots of the dust concentration. Data was log-normally distributed.

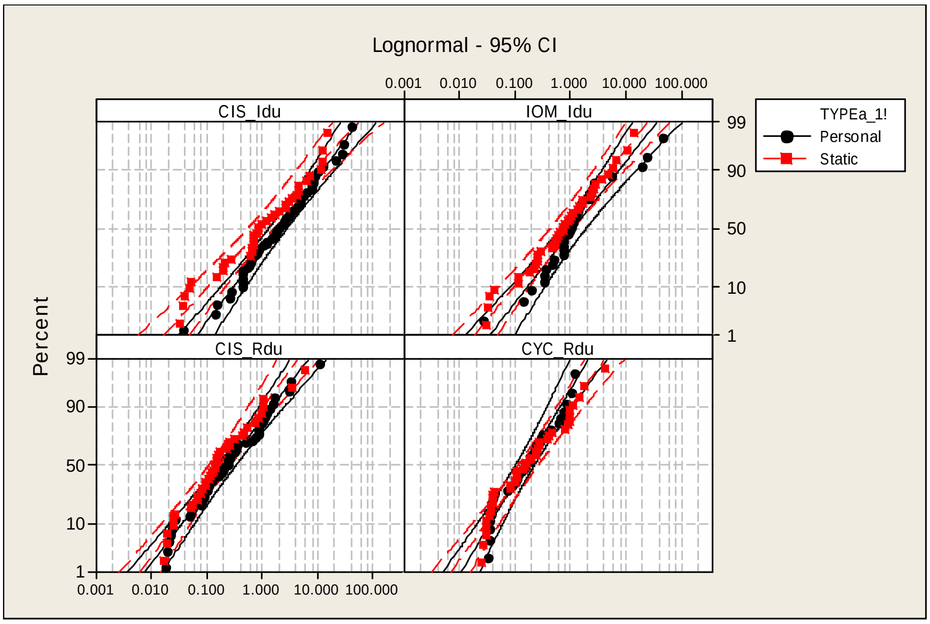

Figure 8 Probability plots of the dust measurements. CIS: conical inhalable sampler, CYC: cyclone, Idu: inhalable dust, Rdu: respirable dust. Dash lines indicated the fitted cumulative distribution (inner line) and confidence intervals (outer lines) based on parameters estimated from the sample

Table 18 shows the inhalable and respirable dust concentrations found in the personal and static paired samples at each company. Appendix 7 shows the dust concentrations for all samples

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Table 18 Personal and static inhalable and respirable dust concentrations (mg.m^{-3}) in each company (paired samples)

PERSONAL

Inhalable fraction		IOM					CIS-I				
Company	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**	**AM**	**GM**	**GSD**	**Min**	**Max**
1	5	1.04	0.820	2.15	0.340	2.46	1.14	0.900	2.09	0.450	2.80
2	4	12.4	2.88	6.41	0.950	46.2	11.2	2.35	19.4	0.040	30.1
3	5	1.02	0.840	2.02	0.320	2.23	1.94	2.59	1.99	0.880	4.21
4	10	5.38	1.18	8.26	0.030	23.6	10.0	3.46	5.68	0.260	43.6
Respirable fraction		**Cyclone**					**CIS-R**				
Company	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**	**AM**	**GM**	**GSD**	**Min**	**Max**
1	5	0.290	0.230	2.05	0.080	0.630	0.370	0.290	2.14	0.100	0.870
2	5	0.160	0.080	3.41	0.030	0.590	0.340	0.110	5.88	0.020	1.24
3	8	0.110	0.080	2.33	0.030	0.230	0.260	0.140	3.5	0.020	1.03
4	5	0.510	0.280	3.56	0.070	1.15	0.490	0.240	4.21	0.050	1.38

STATIC

Inhalable fraction		IOM					CIS-I				
Company	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**	**AM**	**GM**	**GSD**	**Min**	**Max**
1	10	0.540	0.320	3.65	0.030	1.38	1.01	0.440	4.55	0.040	4.79
2	10	3.58	1.8	4.23	0.110	14.3	4.22	1.79	5.67	0.040	12.4
3	5	0.730	0.570	2.24	0.250	1.61	1.05	0.470	5.62	0.030	3.13
4	5	0.450	0.240	4.25	0.030	1.03	2.98	0.730	5.85	0.150	13.1
Respirable fraction		**Cyclone**					**CIS-R**				
Company	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**	**AM**	**GM**	**GSD**	**Min**	**Max**
1	10	0.090	0.070	2.04	0.030	0.180	0.110	0.090	2.25	0.020	0.270
2	15	0.760	0.310	4.63	0.030	4.07	1.02	0.350	5.31	0.020	6.04
3	5	0.160	0.080	3.76	0.020	0.420	0.200	0.130	3.54	0.020	0.450
4	5	0.550	0.300	3.45	0.080	1.73	0.310	0.160	3.27	0.070	1.08

Personal inhalable dust concentrations were much higher that static inhalable concentrations, whereas for the respirable fraction the differences in concentrations between personal and static measurements were smaller.

Personal inhalable dust concentrations varied largely across sites ranging from below the LOD (0.03 mg.m^{-3}) to 46.2 mg·m^{-3} (as measured by the IOM sampling head). AM were 1.04, 12.4, 1.02 and 5.38 mg.m^{-3} for sites 1, 2, 3 and 4, respectively (as measured by the IOM sampling head). Two high inhalable exposure concentrations were observed in companies 2 and 4 (46.2 and 23.6 mg.m^{-3}, respectively, as measured by the IOM head and 30.1 and 43.6 mg. m^{-3} respectively measured by the CIS sampler). Personal respirable concentrations were less variable, ranging from below the LOD (0.03 mg.m^{-3}) to 1.15 mg.m^{-3}. Sites 2 and 3 showed lower concentrations (AM=0.160 and 0.110 mg.m^{-3}) compared to sites 1 (0.290 mg.m^{-3}) and site 4 (0.510 mg.m^{-3}).

Static inhalable concentrations varied less across sites than personal measurements ranging from below the LOD (0.03 mg.m^{-3}) to 14.27 mg.m^{-3}, (as measured by the IOM head), with sites 1, 3 and 4 showing similar concentrations (0.450-0.730 mg.m^{-3}). Site 2 showed considerably higher inhalable concentrations (3.58 mg.m^{-3}). Respirable dust concentrations were comparable across sites (AM ranged from 0.090 for site 1 to 0.760 mg.m^{-3} for site 2, as measured by the cyclone).

The distribution of the ratios of the dust concentrations between samplers (CIS-I: IOM and CIS-R: CYC) is shown in Figure 9. The probability plots showed data fits approximately a log-normal distribution with some very high values of the ratio, especially for the inhalable fraction.

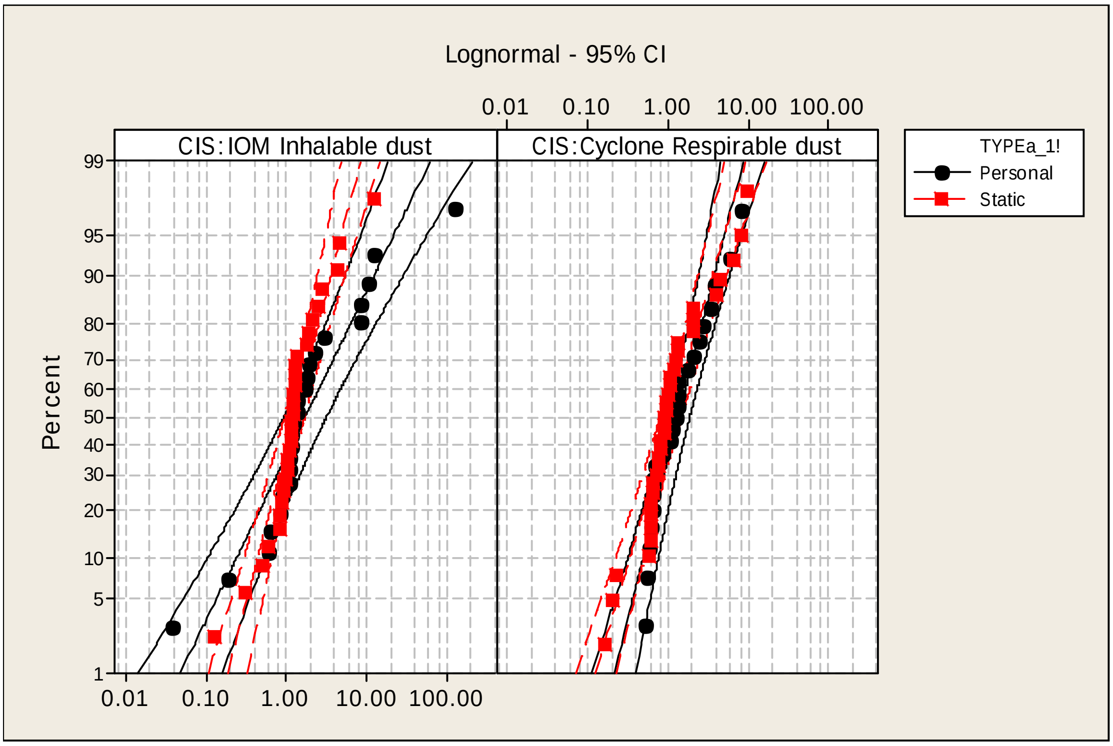

Figure 9 Probability plot of the ratio of dust concentrations between samplers. CIS:IOM ratio of the inhalable fraction of the conical inhalable sampler and the IOM head; CIS:cyclone: ratio of the respirable fraction of the conical inhalable sampler and the HD cyclone. Dash lines indicated the fitted cumulative distribution (inner line) and confidence intervals (outer lines) based on parameters estimated from the sample

Tables 19 and 20 show a summary of the differences in the concentration between samplers, measured as the ratio of the data between samplers for all samples (Table 19), and at each site (Table 20). The regression equation and regression coefficient (R^2) are also presented (Table 19).

The CIS sampler yield higher concentrations than the IOM head and slightly higher concentrations than the HD cyclone, with higher ratios for personal than static samples.
The AM of the ratios for the inhalable fraction (CIS-I: IOM) was 8.07 and 1.85 for personal and static samples, respectively (Table 19). For the respirable fraction (CIS-R: CYC) the AM of the ratios was 1.91 and 1.76 for personal and static samples, respectively. Data was highly skewed as shown by the large differences between the AM and GM, especially for the inhalable personal ratios (CIS-I: IOM). The GSD of the ratios was always > 2.0. Respirable samples showed less variation in the ratios for the different companies.

The high ratio observed for the CIS-I: IOM was driven by a very high ratio (128) observed in company 4. In this sample paired the CIS-I showed a dust mass below the LOD whereas the mass collected on the IOM sampler was above the LOD. Samples with masses below the LOD were assigned half of the LOD value as it is common practice in this type of analysis. However, this resulted in a large difference in the concentrations collected by both samplers.

Figure 10 shows there is a clear dispersion for the CIS-I vs. IOM personal measurements whereas, data followed a linear trend in the case of static CIS-I vs. IOM and personal and static CIS-R vs. cyclone. The differences in the concentrations measured between samplers were mostly systematic as suggested by the R^2 values between samplers: 61% for both personal and static CIS-R vs. cyclone, respectively and 55% and 77% for personal and static CIS-I vs. IOM.

The lower R^2 for the personal CIS-I & IOM and static CIS-R & cyclone suggest other random factors affected the differences between the concentrations sampled with both samplers.

Table 19 Descriptive statistics of the dust ratios between samplers, and least square regression analysis

Personal		**Ratio**			**Regression** Log (CIS-I)=a + b log (IOM)		
Sampler pair	n	AM	GM	GSD	Slope	Intercept	R^2 (%)
CIS-I : IOM	24	8.07	1.76	4.67	0.83*(0.10)	0.36 (0.16)	55
CIS-R : Cyclone	23	1.91	1.35	2.22	0.92* (0.15)	0.14 (0.36)	61

Static		**Ratio**			**Regression** Log (CIS-I)=a + b log (IOM)		
Sampler pair	n	AM	GM	GSD	Slope	Intercept	R^2 (%)
CIS-I : IOM	30	1.85	1.29	2.27	0.99* (0.10)	0.25 (0.16)	77
CIS-R : cyclone	35	1.76	1.08	2.52	0.80* (0.11)	-0.28 (0.25)	61

* $p< 0.001$

Table 20 Descriptive statistics of the ratios of the dust concentration between samplers at each site

Personal samples Sampler pair	**Company**	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**
CIS-I : IOM	**1**	5	1.16	1.09	1.47	0.63	1.72
	2	4	2.87	0.82	9.80	0.04	8.88
	3	5	3.54	1.89	2.95	1.11	13.0
	4	10	15.9	2.93	5.77	0.19	128
CIS-R : Cyclone	**1**	5	1.58	1.26	2.05	0.56	3.87
	2	5	1.84	1.45	2.25	0.59	3.41
	3	8	2.79	1.82	2.63	0.64	8.44
	4	5	0.91	0.84	1.56	0.52	1.35
Static samples Sampler pair	**Company**	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**
CIS-I : IOM	**1**	10	1.52	1.35	1.55	0.87	4.47
	2	10	1.18	0.99	1.89	0.32	2.60
	3	5	1.11	0.82	2.92	0.13	1.94
	4	5	4.62	3.11	2.69	0.93	12.7
CIS-R : Cyclone	**1**	10	1.89	1.19	2.27	0.63	9.89
	2	15	1.89	1.12	2.81	0.16	8.25
	3	5	2.26	1.65	2.45	0.65	4.58
	4	5	0.58	0.53	1.72	0.20	0.82

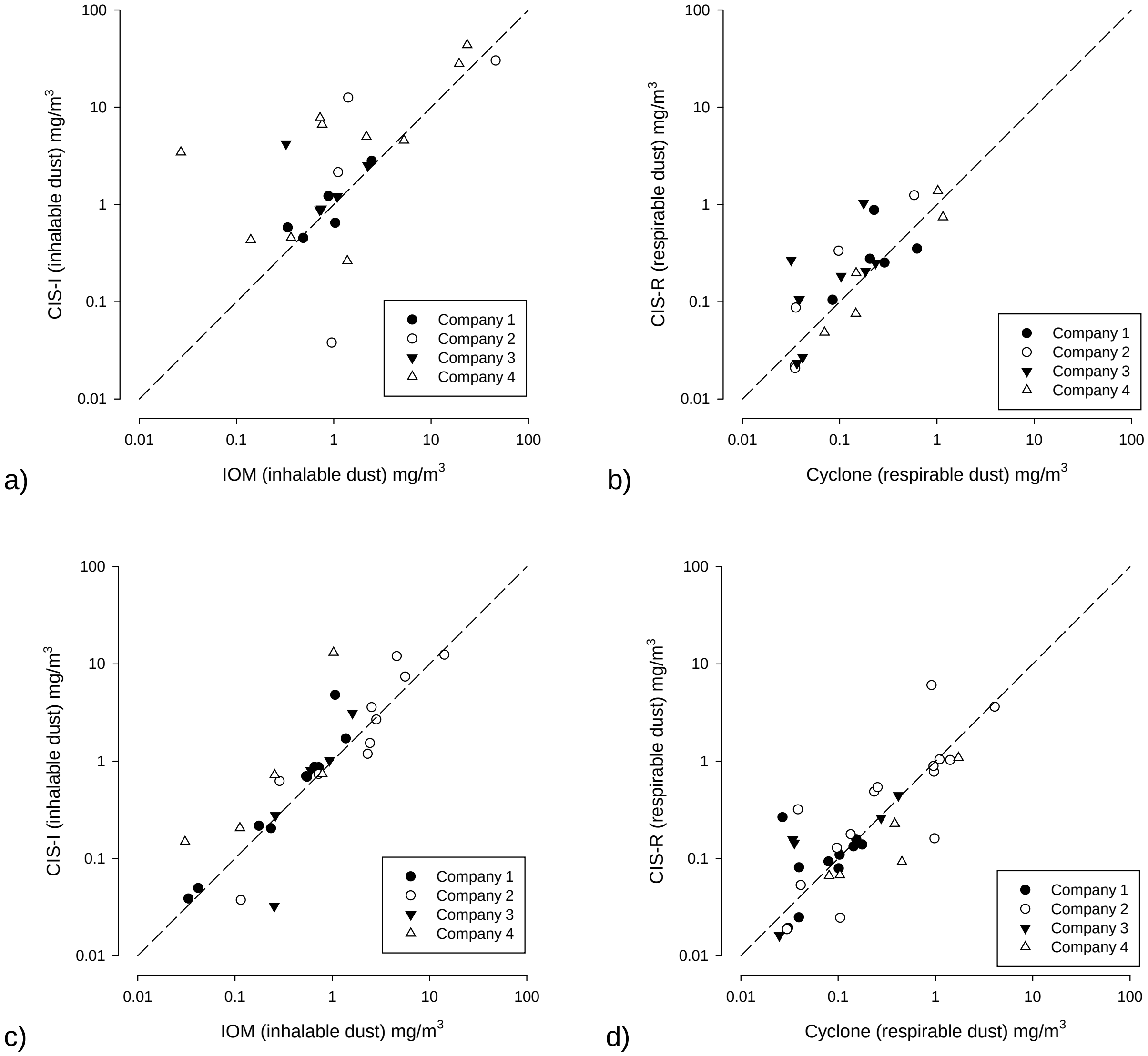

Figure 10 Scatter plot of the inhalable dust concentration in a log-log scale sampled with the Conical Inhalable sampler (CIS) and IOM head and the respirable fraction sampled with the CIS and HD cyclone for personal (a, b) and static (c, d) measurements

7.4.6 Manganese concentrations

The Mn concentrations measured with the different samplers were approximately log-normally distributed (Figure 11).

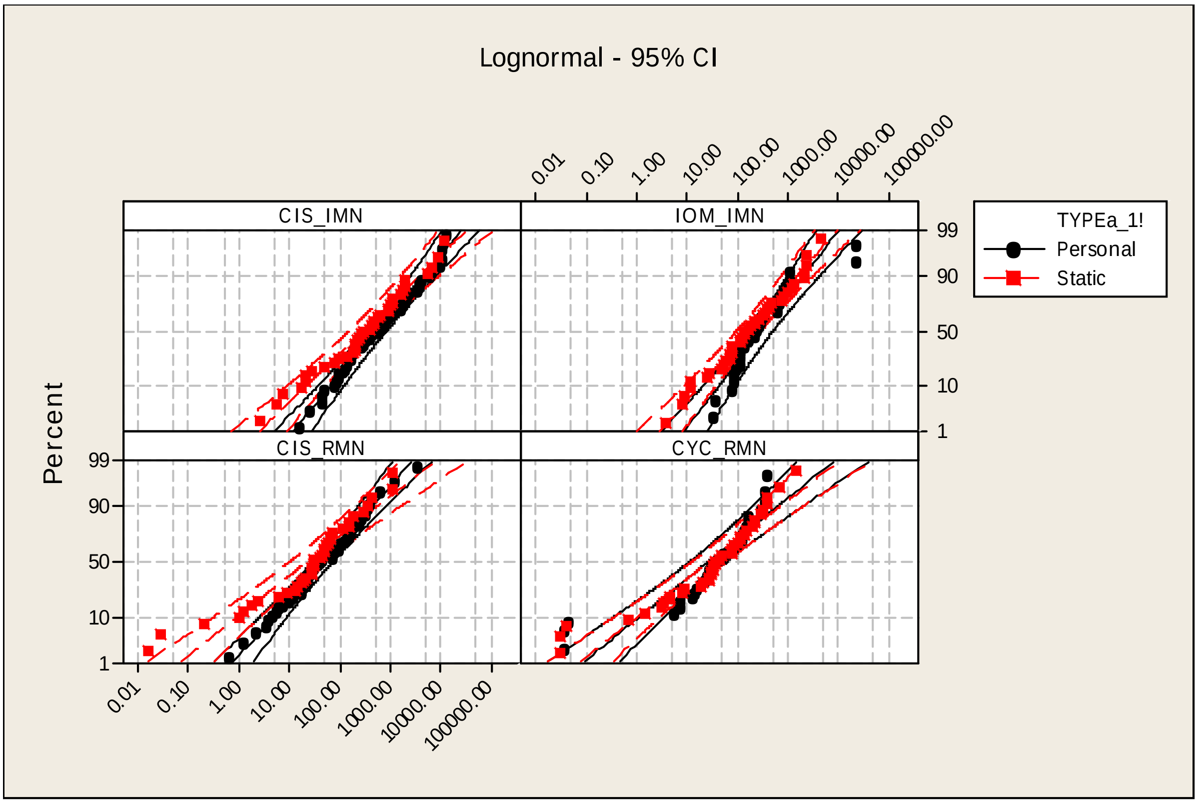

Figure 11 Probability plots of Mn measurements. CIS: Conical Inhalable Sampler., CYC: cyclone, IMN: inhalable Mn, RMN: respirable Mn. Dash lines indicated the fitted cumulative distribution (inner line) and confidence intervals (outer lines) based on parameters estimated from the sample

Table 21 shows a summary of the descriptive statistics for the personal and static inhalable and respirable paired Mn concentrations found at each site. Data for all measurements are shown in Appendix 8.

Table 21 Personal and static inhalable and respirable Mn concentrations (µg.m^{-3}) found in each site (paired samples)

PERSONAL											
Inhalable fraction		**IOM**					**CIS-I**				
Company	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**	**AM**	**GM**	**GSD**	**Min**	**Max**
1	5	305	217	2.52	75.7	793	422	286	2.54	138	1,203
2	4	5,990	869	9.96	112	22,854	4,098	984	14.18	26.8	11,621
3	5	383	254	2.91	85.5	874	826	567	3.07	96.8	1,828
4	10	2,537	255	6.74	33.1	22,912	1,862	576	5.21	49.3	11,405
Respirable fraction		**Cyclone**					**CIS-R**				
Company	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**	**AM**	**GM**	**GSD**	**Min**	**Max**
1	5	119	88.8	2.43	24.9	287	136	104	2.34	30.3	324
2	5	44.1	7.30	24.5	0.04	169	76.8	24.5	5.93	3.40	283
3	8	44.8	6.40	27.77	0.04	154	116	24.8	8.21	1.20	623
4	5	112	43.0	5.19	7.43	349	92.4	36.4	5.46	5.40	222
STATIC											
Inhalable fraction		**IOM**					**CIS-I**				
Company	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**	**AM**	**GM**	**GSD**	**Min**	**Max**
1	10	163	87.0	4.02	7.6	444	282	128.8	4.89	5.4	1,036
2	10	1,321	587	5.44	26.5	4,327	2,732	876	6.69	21.7	9,756
3	5	168	139	1.99	68.3	340	264	113.8	8.90	2.50	498
4	5	111	38.9	6.17	3.6	395	350	97.6	7.81	7.50	1,158
Respirable fraction		**Cyclone**					**CIS-R**				
Company	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**	**AM**	**GM**	**GSD**	**Min**	**Max**
1	10	26.2	11.5	8.81	0.04	78.9	26.8	12.8	6.48	0.20	67.1
2	15	259	57.8	15.7	0.03	1,378	271	91.2	6.38	1.22	1,145
3	5	44.0	29.1	3.16	4.67	110	26.5	5.70	29.6	0.02	67.6
4	5	93.7	33.4	7.82	2.96	207	54.1	18.2	7.68	1.85	153

Personal inhalable Mn concentrations were higher than static inhalable concentrations at all the sites. Personal and static respirable concentrations showed similar AM at sites 3 and 4. At site 1 personal respirable measurements (AM) were much higher than static measurements and at site 2, static respirable measurements showed higher concentrations than personal respirable measurements.

The AM (as measured by the IOM head) of personal inhalable Mn were similar for sites 1 (305 µg.m^{-3}) and 3 (383 µg.m^{-3}) and much higher for sites 2 (5,990 µg.m^{-3}) and 4 (2,537). Sites 2 and 4 showed maximum concentrations values of 22,854 and 22,912 µg.m^{-3}, which lead to the high AM observed. GM were similar for sites 1, 3 and 4 (around 217-254 µg.m^{-3}) and higher for site 2 (869 µg.m^{-3}). Personal respirable concentrations were similar for sites 2 and 3 (AM=44.1 and 44.8 µg.m^{-3}, respectively) and higher for sites 1 (AM=119 µg.m^{-3}) and 4 (112 µg.m^{-3}), as measured by the cyclone.

Static inhalable Mn concentrations (as measured by the IOM head) varied considerable across sites, with AM of 163, 1,321, 168 and 111 µg.m^{-3} for sites 1, 2, 3 and 4, respectively. Respirable static Mn concentrations (AM) were 26.2, 259, 44.0, 93.7 µg.m^{-3}, for sites 1, 2, 3 and 4, respectively. As for personal samples, measurements were highly skewed, as shown by the difference between the AM and GM.

To examine the differences between the samplers the ratio of paired measurements (samples collected simultaneously with the different samplers) was analysed. Figure 12 shows the distribution of the ratios between samplers.

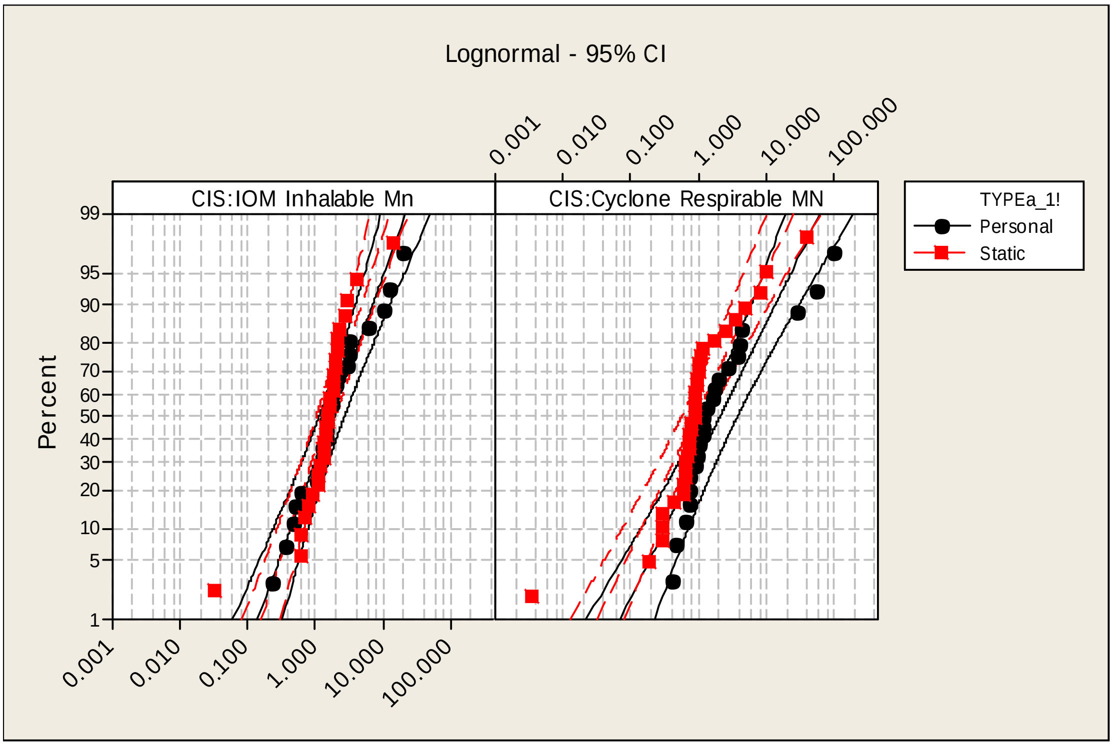

Figure 12 Probability plot of the ratio of the Mn measurements between samplers. CIS:IOM ratio of the inhalable fraction of the Conical Inhalable Sampler and the IOM head; CIS:cyclone: ratio of the respirable fraction of the Conical Inhalable Sampler and the HD cyclone. Dash lines indicated the fitted cumulative distribution (inner line) and confidence intervals (outer lines) based on parameters estimated from the sample

Table 22 shows a summary of the ratio of the concentration between samplers. The least square regression analysis of the data and the regression coefficient are also shown. The scatter plots are shown in Figure 13. A summary of the ratios between samplers observed at each site is shown in Table 23.

The CIS sampler yield higher concentrations than the IOM head and the HD cyclone, especially for personal measurements. There was a large variation in the ratios. The AM of the ratios CIS-I : IOM was 3.39 and 2.10 for personal and static samples, respectively and the AM of the ratios CIS-R : cyclone was 9.53 and 2.64. The GM were 1.79 and 1.47 for personal and static CIS-I : IOM, and 2.08 and 0.91 for personal and static CIS-R : cyclone.

The scatter plots (Figure 13) showed a lilnear trend with less dispersion than that observed for the dust measurements, although some data points clearly deviated from the linear trend (especially those in site 3). As observed for dust, the differences between samplers were systematic as indicated by the high regression coefficients: R^2 = 58% and 76% for personal and static CIS-I: IOM and 76% and 65% for personal and static CIS-R: cyclone, respectively (Table 22). The slopes were not statistically significantly different from 1.

Table 23 shows the Mn ratios for each sample type and company. As was observed for dust measurements, the larger differences between the CIS-I and IOM personal measurements were observed for company 3 and 4, with ratios reaching up to 21.4 in company 3 and 12.7 in company 4. The ratios showed a large variation ranging from 0.41 to 99.3 for personal respirable measurements and from 0.24 to 21.4 for personal inhalable measurements. The ratios of static measurements showed lower ranges with ratios ranging from zero to 14.9 for inhalable measurements and from zero to 40.9 for respirable measurements.

The high ratios between the CIS-R: CYC (ratios of 99.3 at site 2 and 57.9 at site 3 (personal samples) and 40.9 at site 2 (static sample) were due to the Mn collected on the cyclone was below the LOD while the mass collected with the CIS-R was above the LOD. In cases when the mass collected on the filter was below the LOD, half of the LOD value was assigned to those samples. This resulted in a large difference in the CIS and cyclone concentrations yielding the high observed ratios. When these values were removed the AM of the ratio between the CIS-R: CYC was 1.61 instead 9.53.

In once instance the ratio CIS-R: CYC was of 0.003 (site 3 static samples). In this case the CIS sampler had a Mn mass below the LOD, whereas the mass of Mn collected with the cyclone was above the LOD. The corresponding CIS inhalable mass was very low compared to that collected with the IOM, which lead to a ratio CIS-I: IOM of 0.003.

The CIS-I: IOM yield another high ratio in site 3. The much higher mass of Mn collected in the CIS filter compared to the IOM is unclear.

Table 22 Descriptive statistics of the ratios, differences and least square regression analysis of the log-transformed Mn data

Personal		**Ratio**			**Regression** Log (CIS-I)=a + b log (IOM)		
Sampler pair	n	AM	GM	GSD	Slope	Intercept	R^2 (%)
CIS-I : IOM	24	3.39	1.79	2.98	0.74* (0.13)	2.05 (0.78)	58
CIS-R : Cyclone	23	9.53	2.08	4.31	0.56* (0.07)	2.0 * (0.26)	76

Static		**Ratio**			**Regression** Log (CIS-I)=a + b log (IOM)		
Sampler pair	n	AM	GM	GSD	Slope	Intercept	R^2 (%)
CIS-I : IOM	30	2.10	1.47	2.57	1.02* (0.10)	0.28 (0.54)	76
CIS-R : cyclone	35	2.64	0.91	4.21	0.80* (0.10)	0.59 (0.42)	65

* p< 0.001

Table 23 Descriptive statistics of the ratios of the Mn concentration between samplers

Personal samples Sampler pair	**Company**	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**
CIS-I : IOM	**1**	5	1.41	1.32	1.56	0.62	1.82
	2	4	2.27	1.13	4.28	0.24	6.14
	3	5	5.30	2.23	3.58	1.05	21.4
	4	10	3.86	2.26	3.12	0.38	12.7
CIS-R : Cyclone	**1**	5	1.59	1.17	2.31	0.47	4.36
	2	5	21.2	3.36	7.01	0.93	99.3
	3	8	12.6	3.90	5.12	0.41	57.9
	4	5	0.87	0.85	1.31	0.64	1.21
Static samples Sampler pair	**Company**	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**
CIS-I : IOM	**1**	10	1.55	1.48	1.39	0.72	2.41
	2	10	1.85	1.49	2.02	0.62	4.34
	3	5	1.48	0.82	6.05	0.03	2.05
	4	5	4.33	2.51	2.83	1.16	14.9
CIS-R : Cyclone	**1**	10	1.92	1.11	2.69	0.31	8.17
	2	15	4.52	1.58	3.38	0.30	40.9
	3	5	0.51	0.20	10.38	0.003	1.08
	4	5	0.58	0.54	1.51	0.30	0.77

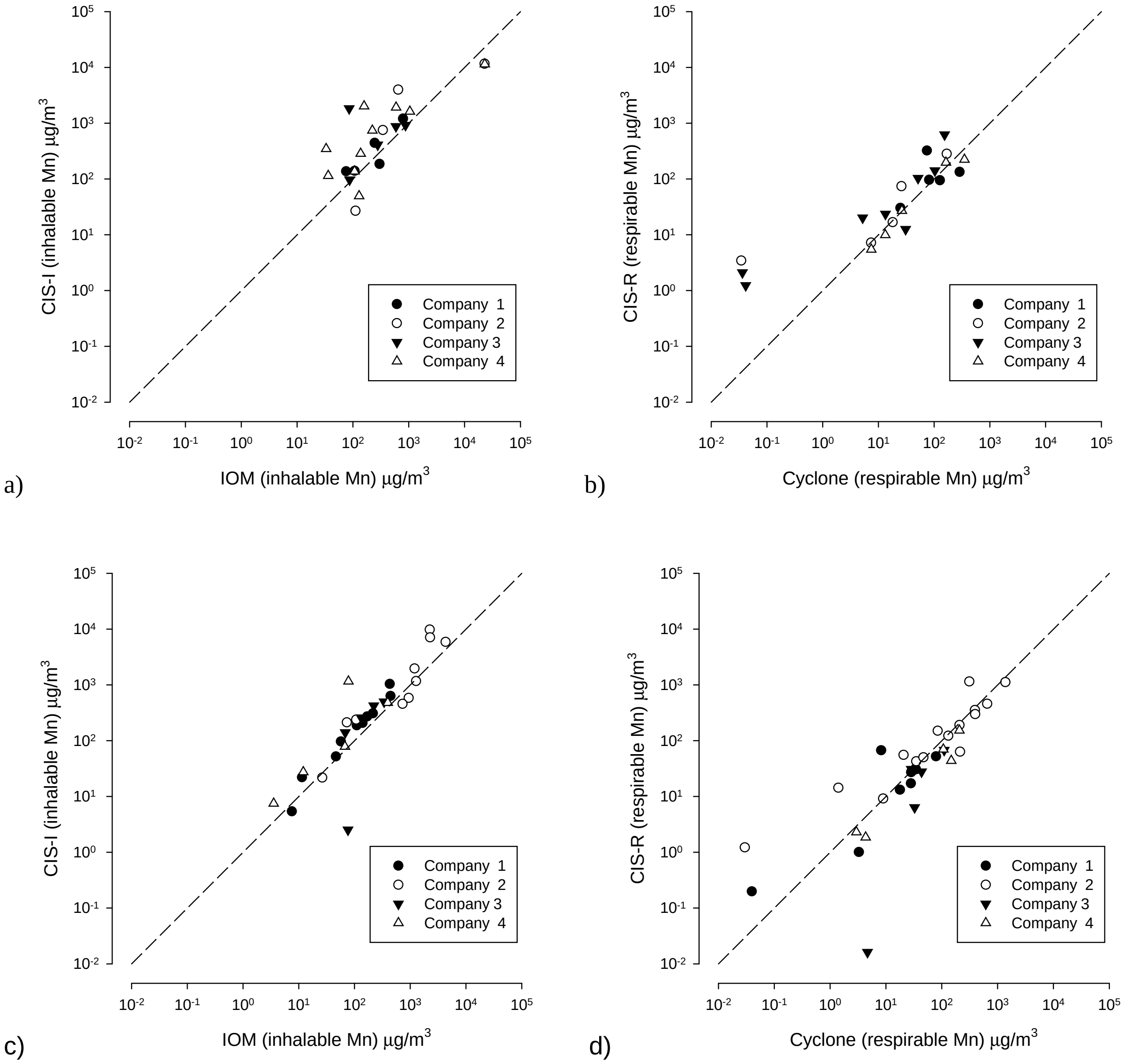

Figure 13 Scatter plot in a log-log-scale of the Mn inhalable concentration sampled with the Conical Inhalable sampler (CIS) and IOM head and the respirable fraction sampled with the CIS and HD cyclone for personal (a and b) and static (c and d) samples.

7.5 MULTIVARIATE ANALYSIS

The data on the dust and Mn ratios between samplers were analysed in more detail to determine whether differences in the results between the samplers were not significant after taking into account effects of site, percentage of respirable dust, sample type (personal and static) and process (presence of dust or presence of dust and fumes) using step-wise regression analyses.

Site was fitted as a random effect and type and process were included as fixed effects in the model. The percent of respirable dust was included as a continuous variable. None of the variables, site, type or process was statistically significant. The analysis of dust showed that for CIS-I: IOM the percentage of respirable dust and site were significant factors ($p < 0.05$). However for the analysis of Mn none of the factors were statistically significant, except site for CIS-R:cyclone for static samples and when both static and personal samples were considered together but not for personal samples.

8 DISCUSSION

The review of the literature indicated that there are few published studies that specifically address sampling for Mn and most of the available information is for other types of dust. The conclusions drawn from studies of other types of dust are expected to be valid for Mn although differences in aerosol particle size distribution will have an important influence on sampler performance. It is not clear how well matched the particle size distribution is for Mn particles in different workplace environments or for Mn aerosols versus other types of aerosol employed in published studies of sampler performance. The findings of the literature review underlined the need for a practical field study to be taken and identified the IOM head (inhalable dust), the HD HD cyclone (respirable dust) and the CIP 10 sampler (dual sampler) as the most promising samplers for further investigation.

Information on current samplers and analytical methods used by the industry as well as contextual information on the Mn surveys were collected through a questionnaire. Twenty-eight Mn metal and metal alloys manufacturing sites located worldwide responded to the questionnaire. We consider this sample size representative of the eventual end-users of the proposed sampling method. Results from the survey revealed that IMnI member companies were supportive of the implementation of a reference method as this will give them “greater confidence and security in any comparisons being made between data collected from different sites and companies as the measurements would be more uniform”. In addition, most of the sites already used the IOM and HD cyclone for collection of the inhalable and respirable dust fraction. Therefore, for most of the sites there would not be any additional cost associated to the implementation of the IOM head and HD cyclone as reference sampling methods. For those sites where other methods are used for regulatory compliance it is still recommended that their sampling strategy includes the proposed samplers to aid comparison throughout the industry and for any future epidemiological studies. It is recommended that measurements collected with the local and proposed methods are undertaken side-by-side. This would allow estimation of a conversion factor between the local and proposed methods, so all measurements can be converted to the corresponding reference method and therefore be compared across all sites. In regard to the contextual information recorded by the sites the results of the questionnaire indicated that few sites fully record contextual information when making occupational hygiene measurements for Mn. In addition to using a reference sampling and analytical method, for each measurement, sites should collect and store appropriate contextual information. The IOM has developed a database “Manganex” to store information on Mn concentrations. The database includes different entry fields to allow retrospective and prospective data gathering. Data can be exported for statistical analysis. It also allows automatic generation of summary reports. The database will be freely available shortly. An example of a sample record sheet with the information required for the Manganex database is shown in Appendix 10.

Results from the literature review together with information collected through the questionnaires lead to the selection of three candidate methods: the IOM head for the inhalable fraction, the HD cyclone for the respirable fraction and the Conical Inhalable sampler (CIS) for the simultaneous collection of both fractions.

The selection criterion was based on the following points:

- The recommended sampler(s) should meet the sampling criteria for measuring the inhalable and/or respirable dust as defined by CEN/ISO/ACGIH.
- The sampling medium should be suitable for analysis of total Mn or Mn compounds.
- The samplers should be appropriate for occupational hygiene purposes (easy to use, not to pose a burden on the wearer, within reasonable cost etc).

The IOM dual sampler was rejected since the PUF had been withdrawn from the market and was not expected to be available during the proposed time period of the sampling surveys. The proposed CIP 10 samplers represented a significant capital outlay. Instead it was agreed an alternative dual sampler: the CIS BGI sampler would be selected. Despite, the CIS sampler being reported to be less extensively used than the CIP and the IOM dual sampler and fewer studies have been published on its performance, this sampler met all the criteria requirements.

The performance of the three samplers was tested in four different Mn manufacturing sites. All IMnI companies were given the opportunity to participate in the study. Four sites, two in the EU and two in Africa were selected for the field study. These sites were considered to represent the Mn industry. Inhalable and respirable Mn measurements were collected simultaneously with the three proposed samplers at approximately five different jobs (personal) and 5 areas (static) representative of Mn exposure in each of the sites.

The results showed that the CIS sampler oversampled in comparison with the concentrations collected with the IOM (inhalable) and HD cyclone (respirable), especially the inhalable fraction for personal samples. The results suggest that the inhalable fraction for personal measurements was subject to a larger random variation than the inhalable static measurements and the respirable fraction, although as shown in the step wise regression sample type was not a significant factor. Personal samples were possibly subject to a greater variability in wind speed and direction, particle size distribution and concentration levels, due to the employees moving across different areas compared to static samplers which were in a fixed point during the entire sampling period. All these factors have been reported to affect sampling performance (Kenny et al. 1997). Therefore, it is not surprising, that personal measurements showed larger variability than static measurements. Sampler orientation also influences on the sampler performance. However, the alternation of the relative position of the samplers in relation to the worker collar and to each other in the case of static measurements should have eliminated any effect on sampling orientation. It should be noted that personal measurements are also influenced by the employee aptitude to wear the samplers correctly, whereas static samplers are not subject to these effects. Small changes in the flow rate, caused by the tubing being bent can have an impact on the final mass collected. Although researches at IOM took all the necessary steps to ensure samplers were wore correctly and at all times, it is not possible to be certain that this was always the case, due to security restrictions to access some areas and the multiple employees carrying samplers. Therefore, concentrations measured in personal samples are thought to be less reliable than area samples in terms of measurement precision and accuracy. Therefore, personal measurements collected in this study are regarded as less precise than static measurements.

The larger differences in the ratio between the CIS-I: IOM for dust and manganese could be related to the fact that deposits on the IOM walls were included in the dust analysis but not in the Mn analysis. The higher ratio between the personal CIS-R: Cyclone for Mn (9.59) compared to dust (1.91) is partly explained by the fact two samples collected with the cyclone showed a mass of Mn below the LOD, whereas the mass collected with the CIS-R sampler was above the LOD. In cases were the mass was below the LOD half of the LOD value was assigned, resulting in a large difference between the concentration collected with both samplers. When these samples with Mn mass below the LOD were removed from the dataset the ratio for dust and Mn were similar (1.91 for dust and 1.61 for Mn).

In contrast to our findings, other studies have reported that the CIS (used only with the filter) undersamples the inhalable dust concentration compared to the IOM sampler, with greater differences for larger particles (>20 µm) in both laboratory studies (Kenny et al. 1997; Kenny et al. 1999; Linden et al. 2000) and field studies (Aizenberg et al. 2001; Thorpe et al. 2007; Predicala et al. 2003). Kerr et al. (2002) in field experiments conducted in the carbon black industry did not found differences between the CIS and IOM samplers, possibly because of the small particle size of black carbon particles. We did not have information on the PSD distribution of Mn particles to judge how much this factor might explain the differences found between both samplers. The only study identified in the Mn industry, on exposure to welding fumes, reported that the CIS sampler slightly overestimated the Mn inhalable concentrations sampled with the IOM head, but the differences were not statistically significant Berlinger et al. (2007). None of these studies used the PU porous foams for separation of the inhalable and respirable fraction. In these studies only the inhalable dust fraction was collected on the filter.

No studies on the comparison of HD cyclone and CIS were found in the peer-reviewed literature.

In addition, the larger differences observed between the inhalable fraction collected by the CIS and the IOM head, compared to the respirable fraction collected with the CIS and HD cyclone could be partly due to the higher uncertainty of analysing foams compared to the analysis of filters. The PUF used in the CIS sampler showed a larger gravimetric instability than the filters used with the IOM and HD cyclone, resulting in a LOD 2 times higher (0.1 mg) compared to that of the filters (0.05 mg). Also, the Mn mass in the laboratory blanks foams was much higher (6.02 µg/ foam), than the Mn mass found in the filters used with the HD cyclone (< 0.1 µg/filter) and IOM head (0.22 µg/filter). Moreover the variability in the Mn content in the blank foams was much larger (SD=2.2 µg / foam) than that found in the glass fibre filters used with the HD cyclone and the IOM head (0.09 and 0.19 µg.filter^{-1}, respectively). The ISO 15202-1:2000 protocol “Workplace air-determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry” states that sampling with PUF can be done as long as the foams have the same low metal content than the filters, which is 0.1 µg of each metal or metalloid of interest per filter. Therefore, the use of the PUF, as provided by the manufacturer, does not seem suitable for Mn analysis. This limitation might be overcome by pre-washing the filters before being exposed however this was not investigated during the course of this study.

Another disadvantage of the CIS sampler is that its use is not as extensive as that of the IOM and HD cyclone. Companies or the corresponding occupational hygiene laboratories should invest in this equipment. In addition, the IOM head and the cyclone are often recommended sampling methods by national authorities and recognised institutes (NIOSH). Although in some countries the OEL are established for the Mn in the total dust fraction and not the inhalable fraction. In these cases it is recommended sites collect a few samples with the proposed method to allow comparison within the industry.

In relation to their usability the three samplers were found easy to use (load and unload of cassettes) and operate, and they did not impose a burden to the wearer. With regard to the costs associated with the different sampling methods, the CIS is obviously more cost-effective since each unit (£50) allows for the collection of both fractions, whereas a set of cyclone and IOM is £85. However, the PUF are substantially more expensive (£130 per 100 pack) than the filters used with the cyclone and the IOM head (£23 and £30, respectively). For example, for the collection of 5 simultaneous measurements the associated cost for using the CIS sampler would be £355, whereas if the IOM head and cyclone were used the cost would be £611 in total.

Based on the results from the field study and the fact that most of the sites already use the IOM sampling head and HD cyclone, these two methods are proposed for collection of the inhalable and respirable fraction of Mn compounds, respectively.

With regard to the chemical analysis of Mn, there are several standard methods suitable for Mn extraction: (e.g. OSHA ID 121 OSHA (2002), OSHA ID 125-G OSHA (1991), NIOSH 7301

(NIOSH, 2003a); NIOSH 7303 (NIOSH, 2003b). These methods used AAS or ICP-AES to quantify Mn. Both techniques are equally suitable for quantification of Mn.

Differences in sampling strategy can be as important as the use of differences samplers. Therefore, to get comparable data, sites should use similar sampling strategies. Samples should be representative of typical exposure concentrations. Consequently, agreement should be taken on the selection of employees and sampling areas and the duration of the sampling period. Information on the sampling survey, including variations in the pump flow rate, exposure controls, exposure pattern, description of the workplace and tasks carried out, and any observations that could influence on the concentrations should be properly recorded.

In this study all samples were analysed at the same laboratory. Investigation on the inter-laboratory differences associated to the analysis of Mn is warranted to properly assess differences in the concentration measured at different sites. Although samples are collected and analysed using the same methods laboratory inter-variability can lead to different results. Therefore, sites should get involved in existing proficiency schemes such as Workplace Analysis Scheme for Proficiency (WASP).

9 CONCLUSION

To date there are not standard methods to assess exposure to Mn dust. Results from a survey among IMnI company's members showed that a range of different samplers and analytical methods are used. The varying performance of different sampling devices may cause a degree of uncertainty when using the sampling results to check compliance with regulatory limits, when the data are used for risk assessment and management purposes or when making comparison of the exposure concentrations at different production sites.

In this study, three candidate sampling devices which meet the CEN/ISO/ACGIH criteria for collection of inhalable and respirable dust were investigated: the CIS dual sampler, the IOM inhalable head and the HD cyclone for measuring the respirable fraction. These samplers were chosen by IMnI and the IOM based on results from a literature reviewed together with a questionnaire survey among IMnI production sites.

Results from the comparison study showed that the CIS sampler overestimated the dust and Mn concentrations collected with the IOM head and the HD cyclone. The main advantage of the CIS sampler is the simultaneous collection of the inhalable and respirable fractions with the same device. This eliminates the need to use two samplers to collect side-by-side samples of the two fractions. Therefore, as only one pump is required errors associated to the use of two different flow rates are eliminated. Cost savings in initial hardware costs can also be achieved, although sampling medium for the CIS (PUF) is more expensive than the filters used with the HD cyclone and IOM.

Therefore, we propose to use the IOM and HD cyclone for sampling of the inhalable and respirable Mn concentrations, respectively based on the following considerations:

- The CIS sampler consistently over-sampled the inhalable concentration compared to the IOM head and cyclone for low and high concentrations.

- The use of the CIS sampler is not as extensive as that of the IOM head and the cyclone according to the findings from the questionnaire distributed to IMnI company's members.

- The metal content of the PUF is much higher than that of the glass fibre filters and above the ISO recommendations for collection of inhalable and respirable airborne particles. The gravimetric LOD for the analysis of PUF is also higher than for the glass fibre filters used with the IOM head and the HD cyclone.

Given that many of the companies who participated in the questionnaire survey indicated that they already use the IOM sampler and a cyclone sampler (and in some instances, both), implementation of these reference samplers should be straight forward. It is acknowledged that for regulatory requirements companies in some countries require the use of other sampler to collect the total, rather than the inhalable fraction. In such instances we would suggest that companies consider the addition and inclusion of a suitable number of inhalable samples within their existing occupational hygiene sampling programme.

The adoption and subsequent collection of Mn samples using the standardised sampling methods will allow the Mn industry to make comparisons between sites, companies and countries, and with appropriate OELs.

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APPENDIX 1: QUESTIONNAIRE

Section 1: Background Information

Number of participating sites per company:

Company A	1 site
Company B	1 site
Company C	1 site
Company D	1 site
Company E	2 sites
Company F	3 sites
Company G	4 sites
Company H	5 sites
Company I	10 sites

Table 1: Responses received for questions 1.5 and 1.6

Question 1.5 and 1.6	Arithmetic Mean	Geometric Mean	Range	Missing data
No. of employees working at the site (exc. office personnel)	272	181	50 - 1309	2
No. of employees at site potentially exposed to manganese*	232	129	0 - 1309	1

*One company had indicated that less than 6 employees would be potentially exposed to manganese therefore a value of 3 was used in order to calculate the means.

Table 2: Question 1.7 Industrial sector for this site

Industrial sector	No. of questionnaires
Mining	4
Production of manganese metal and metal alloys	20
Chemical production of manganese-based chemicals	5
Fabrication (including welding)	2
Other - chemical production of copper based chemicals	1

Section 2: Manganese in workplace air sampling and analytical methods

Table 3: Question 2.1 Do you carry out manganese aerosol sampling for…

…. Manganese aerosols	No. of questionnaires		
	Currently only	Within the past 5 years only	Both currently and within past 5 years
Total	3	3	12
Inhalable	5	3	6
Respirable	6	-	9
Particle size distribution	2*	-	2
Other	respirable crystalline silica**	respirable crystalline silica**	total, dust, respirable dust
Don’t know			1

* 1 stated 0.8um

** No details were provided on whether this is currently or has been previously sampled for

Table 4: Question 2.2 Please list the sampling heads used when sampling for manganese in air. Please also indicate what the sampling head measures.

Sampling head and fraction indicated	**No. responses**	
	Currently	**Within the past 5 years**
Cyclones / respirable		
SIMPEDS cyclone (respirable)	2	2
SKC aluminium cyclone (respirable)	1	1
37mm cassette with cyclone	2	-
Cyclone (respirable)	3	3
Cyclone 25 mm filter	1	-
CIP10R (Capteur Arelco) (respirable)	1	-
CIP R (Capteur Arelco) (respirable)	1	-
Inhalable / total		
CIP 10 I (Capteur Arelco) (inhalable)	1	-
CIP T (Capteur Arelco) (inhalable)	1	-
37mm cassette, added with a ciclon of aluminium (inhalable)	1	1
37mm open face cassette	1	2
37mm cassette (inhalable)	1	1
25mm closed cassette (total)	2	2
Glass fibre head, 37mm (inhalable)	1	-
Millipore cassette (total)	1	2
Closed face polystyrene cassette (inhalable)	1	1
IOM sampling head (inhalable)	2	5
IOM open faced filter holder (25mm)	1	-
IOM head fitted with foam	-	1
Cyclone (inhalable)	2	2
Casella 7-hole samplers (inhalable)	1	1
Other		
Casella Vortex Occupational Environment Pump	1	1
Personal air sample	1	1
low-volume air sampler (total / inhalable) – no further details	1	1
respirable and total dust – no further details	1	2
total dust, respirable dust, zise partik (dust) - no further details	1	1
MP (Millipore) cassette 4 mm inlet	-	1
Pump « BRAVO H » with sampling head screening at 30 µm et suction flow 25 l/min. Bubbling in a solution of HNO3 + H2O2 for the captation of gaseous pollutants.	1	1
25mm cassette, open face. Sampling team composed of: Head of sampling pump suction hose connected to flexible tubing'	1	1
SKC Pump at 2.0 lpm (total dust and manganese); SKC pump at 2.5 lpm (respirable dust and manganese	1	1

Table 5: Question 2.3 Medium used when sampling manganese in air.

…. Manganese aerosols	**No. of questionnaires**		
	Currently only	**Within the past 5 years only**	**Both currently and within past 5 years**
Glass fibre filters	1	-	3
PVC filters	1	1	7
Cellulose ester	3	1	9
Cellulose acetate	-	-	1
Other:	-	-	-
Cellulose nitrate	-	-	1
Membrane filters	-	-	1
Cellulose filter	-	-	1*
Mixed cellulose ester	-	-	1
Don’t know	1	-	-

* did not state if currently or previously used

Table 6: Question 2.5 Analytical methods used to determine manganese in air.

Method	**No. responses**		
	Currently only	**Within past 5 years**	**Both currently & within 5 years**
Gravimetric	-	1	9
ICP	-	-	4
ICP-AES	2	-	9
XRF	-	-	-
AA	5	-	3
AES	-	-	2
Neutron-activation	-	-	-
Colorimetric methods	-	-	-
Other ……	-	-	-
ICP-MS (ICP- mass spectrometry)	-	-	1
Do not analyse for Mn in dust	-	-	1
Don’t know	-	-	-

Table 7: Question 2.6 What standard sampling and analytical methods do you use?

Method	**No. responses**		
	Currently only	**Within past 5 years**	**currently and within 5 years**
MDHS 14/3 General methods for sampling and gravimetric analysis of respirable and inhalable dust	1	-	3
MDHS91 Metals and metalloids in workplace air by x-ray fluorescence spectrometry	-	-	-
MDHS 99 Metals in air by ICP-AES	2	-	1
OSHA ID-121 Metals and metalloid particulates in workplace atmospheres (atomic absorption)	2	-	2
OSHA ID-125G Metal and metalloud particulates in workplace atmospheres (ICP analysis)	1	-	-
NIOSH 0500 Particulates not otherwise regulated, total mass (NIOSH, 1994a)	1	1	1
NIOSH 0600 Particulates not otherwise regulated, respirable (NIOSH, 1998)	1	-	1
NIOSH 7300 Elements by ICP (NIOSH,	3	2	7

Method	**No. responses**		
	Currently only	**Within past 5 years**	**currently and within 5 years**
Other			
National regulations	1	-	-
French Norm NF X 43-275 related to « Quality of the air – Air in working places – Measuring of elements in working places air by atomic spectrometry	-	-	1
NOM-010-STPS-1999	1	-	1
MPL WILAB 4 and NIOSH method 7603 in accordance with AS 2985 (respirable) and MPL WILAB 6,8 and 17 for inhalable in accordance with AS 3640	-	-	2
NOM/10/Proc/52 Secretaria del Trabajop y prevision social Mexico	-	-	1*
Specific method for the external laboratory doing the job	-	-	2
KOSHA Method -1	-	-	1
UNE 81587, with an atomic absorption spectrophotometer	-	-	1
Do not analyse for manganese	-	-	1

* Not known if currently used or within past 5 years

Table 8: Question 2.7 Why do you use the sampling and analytical methods indicated in section 2?

Reason why method is used	**No. of ticked responses**
Specified by company head office	2
Recommended / used by contracted occupational hygienists	15
Recognised standard methods	12
The method is required by national regulations / guidance	13
The are the methods which are available on-site / within company	2
Have been used historically and so continue to use them	5
Greater sensitivity / lower detection limits than other methods	-
Less expensive than other methods	-
Other: Do not analyse for manganese	1
Don’t know	-

Section 3: Measurement collection

Table 9: Questions 3.2 and 3.3 Average number of manganese in air measurements collected annually

Question	**AM**	**GM**	**Range**	**Missing data**
No. personal samples collected annually	91	13	1-1001	5
No. long-term personal samples	*46*	*9*	*1-325*	*4*
No. short term personal samples	*0*	*0*	*0-2*	*34*
No. of static samples collected annually	6	3	0-26	3
No. long-term static samples	*5*	*2*	*0-26*	*4*
No. short term static samples	*0*	*0*	*0-3*	*2*

* Where company had indicated >1000 used a value of 1001 to calculate AM. There was also an instance where a questionnaire had stated plus or minus 200 samples every two years and so used a value of 200 to provide summary statistic. Where a range of 6-8 was provided, a value of 7 was assigned.

Table 10: Question 3.4 Why do you carry out manganese exposure monitoring?

Reason why monitoring undertaken	**No. ticked responses**
Assessment of compliance with occupational exposure limits	25
Assessment of health risk	25
Assessment of control performance	13
Other, please specify *Compliance with legal requirements*	1
Don't know	-

Table 11: Question 3.5 What is your sampling strategy?

	No. responses
Representative	23
Random	6
Task specific	16
Worst case	9*
Don't know	1

* Of which 3 stated that they used NIOSH method

Section 4: Manganese exposure information collected

Table 12: Question 4.15 How are the records of exposure measurements stored?

	No. responses		
	Currently	**Within 5 years**	**Both currently and within past 5 years**
In reports (electronic / hard paper copy)	7	1	19
In a spreadsheet, such as excel	4	2	8
On a computer database, such as Access	3	-	-
In a corporate health surveillance system	2	-	3*
Other, please specify	-	-	-
Don't know	-	-	-

* One stated 'unsure'

Table 13: Questions 4.1-4.14. Please indicate how often the suggested items are recorded

		No. responses				
		Always	**Sometimes**	**Never**	**Don’t know**	**No answer**
4.1	Unique sample ID assigned	26	-	1	1	-
4.2	Date of sampling	28	-	-	-	-
4.3	Worker’s name or identity (personal sampling only)	25	1	1	-	1
4.4	Job title (personal sampling only)	27	1	-	-	-
4.5	Duration of sampling / monitoring	28	-	-	-	-
4.6	Information on tasks /activities carried out during sampling					
	Task names / descriptions	19	8	-	-	1
	Duration of tasks	11	11	3	-	3
	Frequency of tasks	10	7	6	-	5
4.7	Specific location or the worker’s specific place of work	25	2	1	-	-
4.8	The environment where the sample was collected (e.g. confined space, enclosed space, open air)	20	4	3	-	1
4.9	Size of workroom	3	3	17	1	2*
4.10	Type of general ventilation in operation	9	8	8	1	2*
4.11	Information on relevant production processes	17	5	5	-	1*
4.12	Exposure controls at time of monitoring (e.g. enclosure)	14	6	5	1	2*
4.13	Type of personal protective equipment (PPE) worn by workers at the location of monitoring / sampling	18	5	2	1	2*
4.14	Exposure pattern (e.g. intermittent, continuous)	10	8	7	1	2*

* One questionnaire states that ’data available outside of specific sampling events’

Section 5: A standardised method for measuring Mn exposure

Question 5.1 asked about the “Advantages and disadvantages of having a standardised method”. No response was provided in seven questionnaires and one stated that the question was not applicable as they already have a standardised method. The free text provided by the sites is shown below:

‘with accurate sampling, we can check how much damage it can cause and how it effects the human body’

‘Uniformity – Compare “Apples with Apples”. Possible adoption of similar exposure limits in Industry, regardless of country regulated exposure limit provided industry preferred limit is < REL’.

‘Comparing results from other companies, to secure we are doing the right things, and share information and actions to reduce levels when appropriate’

‘Comparing between different companies would be possible and absolutely real’

‘….Possibility to build comparable database of exposure levels between the plants … and more generally between ferro-alloy plants willing to share data’.

‘To look for better alternatives, reducing the levels of manganese exposure and also have better equipment for the workers avoiding to get health infections’

‘To make a confident comparative of the evaluations of the other countries’

‘To be able to make comparisons under the same standardised method internationally’

‘A standardised method would provide uniformity in all areas of monitoring from sampling methods to analysis. This would surely lead to validated internationally accepted exposure standards and enable meaningful comparisons. As there is always much conjecture from employees regarding the health risks associated with working in an environment where exposure to manganese is unavoidable, then data regarding exposure standards could be provided to them with more confidence’

‘Comparison of data will be made easier between the different sites. Benchmarking exercises will become more meaningful if standardised methods are used to collect data. Standardised data will assist is setting standards across the industry’.

‘Benchmarking - for comparison purposes and acceptance of the same OELs within the Mn industry. Uniformity - standardised data will assist in setting standards across the industry’

‘Ensuring all year to year and intra-company results are directly comparable. To ensure sites with less occupational hygiene knowledge (internal or external) move with trends and developments in methods’.

‘Comparison between plants’

'The results would be comparable to using the same parameters all companies'.

‘A standardised method ensures that all the sites are working towards the same goal to eliminate or at least minimise employee exposures. An advantage would be a common methodology to test the effectiveness of engineered controls and PPE. A standardised method supported by the IMnI could also provide an advantage in relating to federal regulatory groups who are developing future manganese exposure standards’.

‘Compare results with other manganese producers. Better communication with the autoroties’.

‘It would enable us to compare our manganese exposure measurements on-site with the other sites of our company and with international manganese exposure standards’.

‘a standardised method gives us the possibility to compare results from measurements to measurements (year to year) and between different plants. There will be consistent measurements from time to time within the plant not dependent on the person responsible for ordering the job or dependent on the external lab doing such a job’.

‘Our plant is quite small. Having a standardised method will allow us to compare with other plants. This is pertinent only if information is shared’.

Responses to Question 5.3 “what are the ‘barriers’ or problems their company may have to adopting a standardised method “

Five questionnaires included no response to this question and eight respondents indicated that they thought there were no barriers to adopting a standardised method. One respondent stated that the question was not applicable to them given that they already use a standardised method. The free text responses to this question are provided below.

The free text to this question is shown below:

‘The external lab in charge of the measurements must have the technical possibility to sample according to the standardised method’

‘The standardised method would need to be user friendly for both the hygiene technician and the persons whose exposure level is being measured. The method should not pose any unforeseen safety risks or impede their ability to complete their work tasks. The standard method should not be cost prohibitive’

‘Individual companies will need to revise their standards and guidance if not aligned to global standard. Competencies in monitoring using new equipment will need to be upgraded. New equipment may need to be sourced. Laboratory services will need to be reviewed. Health and hygiene staff will need to be retrained’

‘Laboratory (analytical) equipment requirements. May require some sites to spend more money either on laboratory equipment or utilising external laboratories’

‘Standard methods have to be approved by actual authorities’

‘Cost implications, capacity of monitoring, technical capacity, accuracy of measuring instruments’

‘If a standardised method is adopted which is less stringent than that of a company's current federal regulatory guideline then extra testing and documentation may be involved to prove compliance to both methods’.

‘If a standardised method is complicated to use, it can give us some challenges’

‘Federal and State regulatory requirements in the USA versus European standards’.

‘Measurement and comparison to OSHA standards / thresholds would remain first priority in determining and selecting appropriate methodologies’.

‘we see no problem using a standard method internally. Perhaps it can be some problem if consuling labs prefer their own methods compared to the standard methods’

‘find a competent laboratory if the method is not a standard for the external company’.

Table 14: Question 5.4 Please rank the following factors in order of priority from 1 to 9, that you think would encourage your company to adopt a standardised method?

	No. of times value ranked…..									
Standardised method…..	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**No info**
Validated	10	1	8	2	1	2	-	-	-	2
easy to use	2	5	2	8	2	4	-	1	-	4
has greater analytical sensitivity / reliability than existing methods	7	2	2	2	4	1	4	1	-	5
associated costs are lower than existing methods used	2	-	2	-	7	1	6	5	-	5
is readily available	3	3	3	3	1	4	2	5	-	4
is adopted by my national health and safety regulator	6	8	5	1	1	-	-	4	-	3
will allow comparison of results with those collected from other sites/companies	6	5	5	3	1	-	5	1	-	2
will allow comparison of our results with national / International exposure standards	3	7	7	3	-	5	-	-	1	2
other reason (please specify)	-	-	-	-	-	-	-	-	1	27

APPENDIX 2: DISCUSSION DOCUMENT AND PRESENTATION – PROPOSED STANDARDISED / REFERENCE METHOD

Standardised method discussion document

Proposal for a standardised method

APPENDIX 3: SAMPLING EQUIPMENT SUPPLIERS

Sampler	Supplier		
	Casella	SKC	JS Holdings
IOM head	✓	✓	
Higgins			✓
Dewell cyclone	✓	✓	
CIS	✓		✓
Web page	http://www.casellameasurement.com/	http://www.skcinc.com/index.asp	http://www.jsholdings.co.uk/index.asp
E-mail	info@casellameasurement.	skcinc@skcinc.com	info@JSHoldings.co.uk
Offices	UK, US, Spain & China	US, UK, South Africa	UK

APPENDIX 4: PROTOCOL FOR SITE VISITS

IOM protocol for site visits.pdf

APPENDIX 5: EMPLOYEE ACTIVITY QUESTIONNAIRE

This appendix provides an example of the employee activity questionnaire which we would hope the personal monitoring participates can complete. We would greatly appreciate any comments you may have with respect to this and for this questionnaire to be translated into French.

ID :	
Job title :	
Pump/sampler numbers *(to be completed by IOM)* :	
Time to fill in the questionnaire:	
What production areas/jobs have you done today?	

Atelier	**Production areas**	**Time (min.)**

During your shift has you noticed something unusual in regard to dust exposure?	**Yes**	**No**

APPENDIX 6: CLASSFICATION OF PROCESES ACCORDING TO ABSENCE OR PRESENCE OF FUMES AND DUST

Site	Area/job title	Type of process
1	Foreman (all production areas)	dust & fumes
1	Foreman-warehouse	dust
1	Fork-lift driver	dust
1	Mechanical Maintenance	dust & fumes
1	Mn_3O_4 production	dust & fumes
1	MnO packing	dust
1	MnO production	dust
1	Mn_3O_4 packing (end of packing line)	dust
1	Staff (resting) room in MnO production area	dust
2	Furnace controller	dust & fumes
2	Sinter Operator	dust
2	Tapping operator	dust & fumes
2	Crushing operator	dust
2	Control Room operator	dust
2	Driver (tapping area)	dust & fumes
2	Mechanic (all areas)	dust & fumes
2	Production manager	dust & fumes
2	Control room	dust
2	Sintering	dust
2	Tapping	dust & fumes
2	Electrode area	dust
2	Sinterisation	dust
2	Crushing and storage of final product	dust
3	Forklift driver	dust
3	Powder operator	dust
3	Briquette operator	dust
3	Knock off of Mn in electrolytic plate	dust
3	Cell house grader/sampler (take samples from the Mn solution)	dust & fumes
3	Electrolitic cell maintenance	dust
3	Funkey driver	dust
3	Filtering of the Mn solution	dust & fumes
3	Oremill controller	dust
3	Stores supervisor	dust
3	Calciner	dust & fumes
3	Mn3O4 production	dust & fumes
3	Furnace area	dust & fumes
3	Storage of personal protection equipment	dust

Site	Area/job title	Type of process
3	Redler catwalk, area above calciner	dust & fumes
3	Crushing area	dust
3	Topside of cell house	dust
4	Crane driver	dust & fumes
4	Laboratory	dust
4	Control room operator	dust
4	Pellelizing	dust
4	Crusher	dust
4	Metal tapper	dust & fumes
4	Casting bay	dust & fumes
4	Tapper	dust & fumes
4	Gas plant controller	dust & fumes
4	Forklift driver	
4	Tippler	dust & fumes
4	Crane operator	dust & fumes
4	Tapping	dust & fumes
4	Slag crushing & stockpiling area	dust
4	Casting onto floor/skimming	dust & fumes

APPENDIX 7: DUST CONCENTRATIONS

PERSONAL												
Inhalable fraction	**IOM**						**CIS-I**					
Company	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**	**N**	**AM**	**GM**	**GSD**	**Min**	**Max**
1	8	1.13	0.87	2.13	0.34	2.63	13	1.35	0.96	2.31	0.29	4.91
2	6	8.77	2.28	4.41	0.95	46.2	10	7.38	2.08	8.87	0.04	30.09
3	5	1.02	0.84	2.02	0.32	2.23	14	3.51	1.93	3.10	0.14	21.7
4	11	4.91	1.00	7.98	0.03	23.6	18	7.41	3.12	4.24	0.26	43.55
Respirable fraction	**Cyclone**						**CIS-R**					
Company	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**	**N**	**AM**	**GM**	**GSD**	**Min**	**Max**
1	10	0.34	0.23	2.72	0.04	0.84	13	0.23	0.15	2.64	0.024	0.87
2	6	0.15	0.08	3.07	0.03	0.58	10	1.64	0.27	9.13	0.02	11.1
3	9	0.10	0.07	2.31	0.03	0.23	14	0.23	0.15	2.72	0.02	1.03
4	7	0.47	0.30	2.86	0.07	1.15	18	0.82	0.37	4.49	0.02	3.36
STATIC												
Inhalable fraction	**IOM**						**CIS-I**					
Company	**N**	**AM**	**GM**	**GSD**	**Min**	**Max**	**N**	**AM**	**GM**	**GSD**	**Min**	**Max**
1	15	0.94	0.44	3.74	0.03	6.53	11	0.98	0.45	4.23	0.04	4.79
2	12	3.22	1.34	5.83	0.03	14.3	16	4.96	2.63	4.44	0.04	16.1
3	5	0.73	0.57	2.24	0.25	1.61	7	1.05	0.43	5.85	0.03	3.13
4	9	2.16	0.74	5.97	0.03	10.5	5	2.98	0.73	5.85	0.15	13.1
Respirable fraction	**Cyclone**						**CIS-R**					
Company	**n**	**AM**	**GM**	**GSD**	**Min**	**Max**	**N**	**AM**	**GM**	**GSD**	**Min**	**Max**
1	14	0.12	0.09	2.25	0.03	0.27	11	0.11	0.09	2.17	0.02	0.27
2	16	0.71	0.27	4.90	0.03	4.07	16	1.02	0.37	5.14	0.02	6.04
3	5	0.16	0.08	3.76	0.02	0.42	7	0.16	0.09	3.37	0.02	0.44
4	6	0.59	0.36	3.25	0.08	1.73	5	0.31	0.16	3.27	0.07	1.08

APPENDIX 8: MN CONCENTRATIONS

PERSONAL												
Inhalable fraction	**IOM**						**CIS-I**					
Company	**N**	**AM**	**GM**	**GSD**	**Min**	**Max**	**N**	**AM**	**GM**	**GSD**	**Min**	**Max**
1	8	369	243	2.61	76	1,107	13	520	316	2.82	77	2,068
2	6	4,152	686	6.31	112	22,854	10	3,274	870	8.88	27	11,621
3	5	383	254	2.91	86	874	14	1,916	626	5.84	17	13,268
4	11	2,315	231	6.29	33	22,911	18	2,130	655	5.25	49	11,405
Respirable fraction	**Cyclone**						**CIS-R**					
Company	**N**	**AM**	**GM**	**GSD**	**Min**	**Max**	**N**	**AM**	**GM**	**GSD**	**Min**	**Max**
1	10	149	93.8	3.0	14.60	372	13	77	43.0	3.2	4	324
2	6	42	9.3	18.6	0.03	169	10	453	49.7	12.7	1	3,538
3	9	46	8.0	24.2	0.04	154	14	89	27.4	5.6	1	623
4	7	102	46.2	4.2	7.40	349	18	204	73.5	5.1	5	1,309
STATIC												
Inhalable fraction	**IOM**						**CIS-I**					
Company	**N**	**AM**	**GM**	**GSD**	**Min**	**Max**	**N**	**AM**	**GM**	**GSD**	**Min**	**Max**
1	15	288	109	4.40	8.0	2153	11	275	135	4.54	5	1037
2	12	1,209	441	7.25	9.0	4327	16	2,944	1221	5.07	22	11,907
3	5	168	139	1.99	68	340	7	334	118	8.50	3	999
4	9	432	122	7.46	4.0	2075	5	350	98	7.81	8	1,158
Respirable fraction	**Cyclone**						**CIS-R**					
Company	**N**	**AM**	**GM**	**GSD**	**Min**	**Max**	**N**	**AM**	**GM**	**GSD**	**Min**	**Max**
1	14	49	15.5	9.6	0.0	280	11	26	13.3	5.9	0.2	67
2	16	243	36.1	26.1	0.0	1,379	16	276	99.2	6.2	1.2	1,145
3	5	44	29.1	3.2	5.0	110	7	22	3.2	33.6	0.02	68
4	6	94	40.0	6.6	3.0	207	5	54	18.2	7.7	1.9	153

APPENDIX 9: STEP WISE REGRESSION: P-VALUES

DUST

CIS : IOM

Variable	All samples	Personal	Static
% respirable. dust	<0.001	0.017	0.003
Site	0.002	0.163	0.027
Process	0.648	0.463	0.881
Sample type	0.289		

CIS : Cyclone

Variable	All samples	Personal	Static
% respirable. dust	0.243	0.904	0.231
Site	0.391	0.886	0.369
Process	0.244	0.370	0.082
Sample type	0.346		

MANGANESE

CIS : IOM

Variable	All samples	Personal	Static
% respirable. dust	0.050	0.280	0.120
Site	0.051	0.392	0.123
Process	0.784	0.873	0.881
Sample type	0.585		

CIS : Cyclone

Variable	All samples	Personal	Static
% respirable. dust	0.813	0.841	0.710
Site	0.007	0.251	0.029
Process	0.515	0.612	0.588
Sample type	0.295		

APPENDIX 10: MANGANEX SAMPLING RECORD SHEET

Manganese Exposure Database System – [KEY FIELDS ON PAGE 1WILL BE FILLED WITH ALREADY DEFINED SURVEY PLANNING DATA]

General survey planning details

Survey ID/Ref no

Full survey name:

Start date:

End date:

Commissioned by:

Survey manager

Reason:

Sampling Strategy:

If random, applies to: Day ☐ Worker ☐

Sample types included Personal: ☐ Static/Fixed: ☐

Sample durations: Whole/Part shift: ☐ Short term: ☐ Task specific ☐

Service providers (if used): Surveyor:

Analyst:

Sampling and analytical methods

Dust Fraction	Sampling Device	Sampling Medium	Analyte	Analytical method & technique	LOD (Units)	Note

Processes covered by survey

Process name	Process type	Batch Frequency	Duration	N Operators	Primary Controls	Note

Workplaces covered by survey

Workplace name	Workplace type	Size category	Ventilation type	Note

Individual Static Sample Details

Static Samples

Sample ID: ☐ Sampling device: ☐ Sampling media: ☐

Static sample source proximity Near (< 1m) ☐ Far (> 1m) ☐

Sample date: ☐

Start time	End time	Break duration (min)	Break sampled Y/N	Sample duration	Start flow rate	End flow rate	Mean flow rate	Note
:	:							

Tasks undertaken

Task	Duration (min)	Controls type	Note

Workplaces visited

Workplace	Duration (min)	N Workers	Note

Process undertaken

Process	Duration (min)	N Workers	Note

General exposure pattern:

Exposure conditions:

Analytical results

Substance	Fraction	Analytical method	LOD	Result	Result units	Sample vol	Concentration	Note

Individual Personal Sample Details **Personal Samples**

Sample ID: Sampling device: Sampling media:

Sample Date

Start time	End time	Break duration (min)	Break sampled Y/N	Sample duration	Start flow rate	End flow rate	Mean flow rate	Note
:	:							

For personal samples – Employee information

Staff ID	Forename	Surname	Job Title	Shift start time	Shift finish time	Note

Tasks undertaken

Task	Duration (min)	Controls in use	RPE used	Protn factor	PPE Gloves	PPE Clothing	Note

Workplaces visited

Workplace	Duration (min)	Number of Workers	Note

Process undertaken

Workplace	Duration (min)	Number of Workers	Note

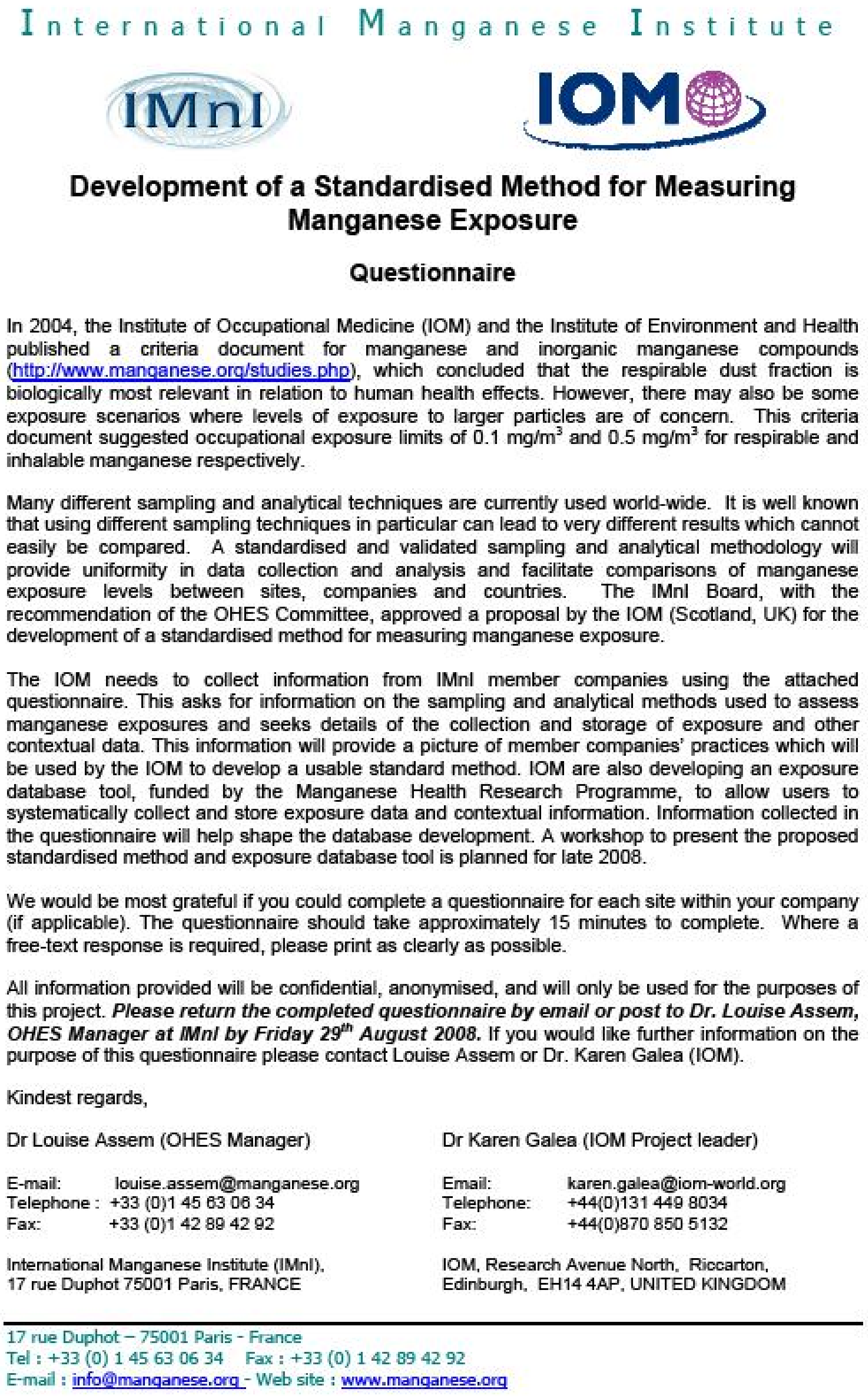
General exposure pattern: ☐

Exposure conditions: ☐

Personal workrate: ☐

Analytical results

Substance	Fraction	Analytical method	LOD	Result	Result units	Sample vol	Concentration	Note



International Manganese Institute

Development of a Standardised Method for Measuring Manganese Exposure

Questionnaire

In 2004, the Institute of Occupational Medicine (IOM) and the Institute of Environment and Health published a criteria document for manganese and inorganic manganese compounds (http://www.manganese.org/studies.php), which concluded that the respirable dust fraction is biologically most relevant in relation to human health effects. However, there may also be some exposure scenarios where levels of exposure to larger particles are of concern. This criteria document suggested occupational exposure limits of 0.1 mg/m^3 and 0.5 mg/m^3 for respirable and inhalable manganese respectively.

Many different sampling and analytical techniques are currently used world-wide. It is well known that using different sampling techniques in particular can lead to very different results which cannot easily be compared. A standardised and validated sampling and analytical methodology will provide uniformity in data collection and analysis and facilitate comparisons of manganese exposure levels between sites, companies and countries. The IMnI Board, with the recommendation of the OHES Committee, approved a proposal by the IOM (Scotland, UK) for the development of a standardised method for measuring manganese exposure.

The IOM needs to collect information from IMnI member companies using the attached questionnaire. This asks for information on the sampling and analytical methods used to assess manganese exposures and seeks details of the collection and storage of exposure and other contextual data. This information will provide a picture of member companies' practices which will be used by the IOM to develop a usable standard method. IOM are also developing an exposure database tool, funded by the Manganese Health Research Programme, to allow users to systematically collect and store exposure data and contextual information. Information collected in the questionnaire will help shape the database development. A workshop to present the proposed standardised method and exposure database tool is planned for late 2008.

We would be most grateful if you could complete a questionnaire for each site within your company (if applicable). The questionnaire should take approximately 15 minutes to complete. Where a free-text response is required, please print as clearly as possible.

All information provided will be confidential, anonymised, and will only be used for the purposes of this project. ***Please return the completed questionnaire by email or post to Dr. Louise Assem, OHES Manager at IMnI by Friday 29th August 2008.*** If you would like further information on the purpose of this questionnaire please contact Louise Assem or Dr. Karen Galea (IOM).

Kindest regards,

Dr Louise Assem (OHES Manager)

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(Double click to view full questionnaire)