`

International Antimony Association

Guidance for the monitoring of antimony in inhalable and respirable airborne particulate matter in workplace atmospheres

Part 1: Sampling and analysis

Version 1.2

June 2019

VERSIONS

Version	Date issued	Remarks
1.1	19.02.2019	Public version
1.2	09.04.2019	Main updates as follows: • Section 3 and Section 13 – Updated to reflect recommended sample preparation and analysis methods. • Section 5 – Addition of text concerning the selection of 'worst-case exposure' groups. • Section 7 & 8 – Correction on filter sampling media to be used. • Section 8 & 10 – Addition of text to highlight need for use of intrinsically safe pumps in explosive environments. • Section 11 – Addition of text concerning sample duration, with due consideration of analytical reporting limits. • Minor spelling and formatting issues also corrected

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

Contents

International Antimony Association (VZW)

Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com

www.antimony.com

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

ABBREVIATIONS

µm	Micrometer
AIHA	American Industrial Hygiene Association
As	Arsenic
ACGIH	American Conference of Governmental Industrial Hygienists
CEN	Comité européen de normalisation (European committee for standarization)
C(E)S	Contributing (Exposure) Scenario
D_{50}	Particle diameter corresponding to 50% sampling efficiency.
ECHA	European Chemicals Agency
ES	Exposure Scenario
HSE	Health and Safety Executive (UK)
i2a	International Antimony Association
ICP AES	Inductively Coupled Plasma Atomic Emission Spectrometry
IOM	Institute of Occupational Medicine
ISO	International Standard Organization
l/min	litres per min
LOD	Limit of Detection
LOQ	Limit of Quantification
MDHS	Methods for the Determination of Hazardous Substances
mm	Millimetre
NIOSH	National Institute for Occupational Safety and Health (US)
NTP	National Toxicology Program
OC	Operational Conditions
OEL	Occupational Exposure Limit
OELV	Occupational Exposure Limit Value
Pb	Lead
PPE	Personal Protective Equipment
REACH	Registration, Evaluation, Authorisation and Restriction of Chemicals
RMM	Risk Management Measures
RPE	Respiratory Protective Equipment
Sb	Antimony
SEG	Similar Exposure Group
TWA	Time Weighted Average

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

1. INTRODUCTION

Toxicological studies of antimony (Sb) in its various chemical forms have revealed that high exposure to Sb can yield, among others, lung toxicity. Due to this 'hazard', regulatory authorities have scrutinized Sb to assess the actual 'risk' related to the production and/or use of Sb substances. A chemical is considered to pose a risk where those producing or using it are exposed to it in quantities above the dose at which the hazard is known to manifest itself. A proper risk assessment therefore requires a good knowledge of both the dose associated with hazard expression, and the exposure levels.

The lack or insufficiency of exposure data about Sb in producer and downstream user workplaces triggers the need to develop a number of assumptions and make various extrapolations when assessing the possible risk related to the production and/or use of Sb substances. In the absence of an appropriate exposure database, agencies and authorities deriving safe exposure levels and deciding on other relevant risk management measures (RMMs) for Sb substances have to assume the worst-case: highest exposure, i.e. highest risk.

The National Toxicology Program (NTP) Toxicology and Carcinogenesis Studies of Antimony Trioxide published in December 2017 (NTP, 2017) provide new toxicological evidence expected to trigger a wave of reviews of the classifications and workplace limits in place so far for antimony trioxide and perhaps other antimony compounds. Unless an appropriate exposure dataset is available to inform the authorities undertaking these reviews, there is a high chance that revised regulatory requirements will be over-conservative and inefficient due to worst case assumptions being made about exposures in the workplace.

Exposure to substances hazardous to health may occur in the workplace in the form of aerosols. The term 'aerosol' is used to describe any suspension of particles in air, and most aerosols consist of a wide range of particle diameters. It is possible to define aerosol size fractions that relate to the region of the respiratory tract where they are most likely to deposit. The convention for these size fractions is described in ISO 7708 (ISO, 1995) or BS EN 481 (BSI, 1993) (Figure 1).

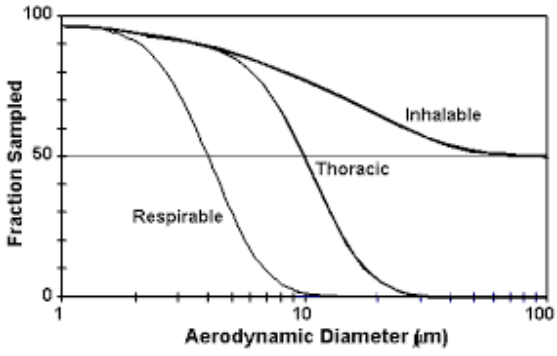

Figure 1. ISO/BS EN sampling conventions

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

These are the inhalable, thoracic and respirable size fractions:

1. Inhalable fraction – this approximates to the fraction of airborne material that enters the nose and mouth during breathing, and is therefore available for deposition in different regions of the respiratory tract (D_{50}[1] of sampler = 100 µm).
2. Thoracic fraction – this is the smaller sub-fraction of inhaled airborne material penetrating beyond the larynx.
3. Respirable fraction – this is the inhaled airborne material that penetrates to the lower gas exchange (alveolar) region of the lung, (D_{50} of sampler = 4 µm).

The NTP studies confirm that the adverse effects caused by Sb in the lung are very likely mediated by exposure to particles able to reach the alveoli (< 4 µm), or so-called 'respirable' forms of Sb. The current practice however, is to monitor 'inhalable' forms (< 100 µm). There is hence a need to gather both inhalable exposure data (to document the current exposure for a broader part of the value chain) and respirable exposure (in anticipation of limits which are/will be defined for respirable particles based upon the NTP studies).

[1] Particle diameter corresponding to 50% sampling efficiency.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

2. i2a's WORKPLACE EXPOSURE MONITORING CAMPAIGN

i2a's Product Stewardship program includes a Workplace Exposure Monitoring Campaign aimed to provide relevant[2] and reliable[3] exposure data to expert agencies and authorities[4] in charge of assessing the risk associated with the production and use of Sb chemicals on the workplace. Provision of an appropriate exposure database will avoid worst-case assumptions with respect to exposure intensity and the particle size distributions that dictate patterns of pulmonary deposition. Such information will guide experts and regulators towards the most proportionate and efficient opinions and decisions regarding the impacts of, and limits upon, occupational exposures.

The aims of i2a's exposure monitoring campaign are to:

- Collect relevant and reliable personal Sb[5] exposure data from representative sites throughout the value chain (covering production and main uses), to be used by expert agencies and authorities in assessing safe production and use, and deriving the most appropriate exposure level that should be implemented on workplaces where Sb substances are produced and/or used.
- Document the current Sb exposure levels in workplaces where Sb substances are produced and/or used, and quantify this exposure in both the inhalable and the respirable fractions of the airborne particulate matter.
- Demonstrate compliance with current and recently revised occupational exposure levels (e.g. in Japan or in Germany), as well as expected future revisions of these (e.g. ACGIH).
- Develop sector recommendations for the continued prevention, minimization and control of Sb exposure in workplaces where Sb substances are produced and/or used.

To achieve these aims, it is vital that as wide a range and number as possible of Sb producer and downstream user sites participate in the campaign. The collection of inhalable and respirable Sb personal exposure data following a centralized and harmonized approach is key to identify the most proportionate and efficient RMMs.

[2] Relevant: Related specifically to Sb
[3] Reliable: Trustworthy, credible, and valid; generated and collected on the basis of documented and repeatable protocols
[4] E.g.: IARC, NTP, FDA, EPA, ACGIH, NIOSH, OSHA, ECHA, SCOEL, and equivalent bodies worldwide
[5] Samples will also be analyzed for lead (Pb) and arsenic (As) as potential contaminants, with the results of these measurements also being summarized and reported.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

3. REMIT OF GUIDANCE AND INTENDED AUDIENCE

The 'Guidance for the monitoring of antimony in inhalable and respirable airborne particulate matter in workplace atmospheres' is split into two Parts.

Part 1 of this guidance provides a practical description of the methods and practical steps to sample Sb in airborne particulate matter in the workplace atmosphere of the producers and users of Sb substances. The proposed methods have been selected with due consideration of a number of official standards and documents, as well as workplace air monitoring guidance documents (e.g. HSE, 2014; ISO 15202-2, 2012a; TRGS 402, 2010; BS EN 482:2012+A1:2015). Consideration has also been given to published literature, which have reported comparisons between samplers for the more general measurement of dust in workplaces (e.g. Aizenberg et al, 2001; IOM, 2011).

Whilst reference to the laboratory analysis methods of the collected personal samples is also provided within this guidance document, readers are directed to the following copyrighted ISO standards for more information:

- ISO 15202-2 Workplace air -- Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry -- Part 2: Sample preparation (Annex G) (ISO, 2012b)
- ISO 30011:2010 F Workplace air -- Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma mass spectrometry (ISO, 2010)

These standards provide the required level of detail for sample extraction and analysis methodologies to be employed. Collected air samples must be analyzed by competent analytical laboratories experienced in the recommended analytical techniques (again, without such rigor, generated data may not uphold regulatory scrutiny and validation). Further information on this subject is provided in later sections of this guidance document.

Part 2 of this guidance will focus on the collection of relevant supporting contextual information to inform the sample results. This will include sampling and analytical information as well as key information on the activities, operational conditions (OC), risk management measures (RMM) etc. that were in place at the time of the measurement campaign. Part 2 of the guidance document will provide details of the Excel templates to be completed during the campaign, as well as guidance on how to input and return the provided data.

The steps and practical recommendations described in Parts 1 and 2 of this Guidance document are aimed at company sites willing to participate in the exposure data collection starting in 2019 and running until 2021.

This guidance document is intended for use by persons suitably trained and competent in occupational hygiene / occupational exposure assessment practice and particularly in the collection of personal exposure samples and relevant supporting contextual information (absence or insufficient contextual information makes data unusable in a regulatory context). The collection of personal exposure measurements by personnel inexperienced in good occupational hygiene practice is not recommended. Indeed, TRGS 402 (2010) states that *"employers who do not have access within their company to the necessary knowledge and essential prerequisites MUST delegate knowledgeable external bodies to identify and assess the inhalation exposure*". In instances where companies do not have in-house personnel, they should seek expert advice and support from the Institute of Occupational Medicine (IOM), i2a's contractors who are assisting with the measurement campaign, or other occupational hygiene experts.

It should be noted that the use of sampling equipment supplier names within later sections of this guidance document does not constitute endorsement by i2a.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

4. WHAT IS PERSONAL SAMPLING?

Personal samples are preferred (and are requested for the purpose of this measurement campaign) to area or static samples to evaluate the exposure of workers to airborne chemicals because they are more representative of what workers are exposed to.

Personal sampling requires workers to wear personal sampling devices which collect samples of the air present in their breathing zone (about 20-30 cm hemisphere around the nose and mouth) usually positioned around the lapel, upper chest region (Figure 2), wherever they work on the site, and whatever activity(ies) they are involved in. Personal samplers should be positioned within the indicated breathing zone regardless of whether respiratory protective equipment (RPE) is being worn during the work activities, being positioned above other RPE or other personal protective equipment (PPE) so that it is not covered.

Figure 2. Illustration of sampler placed within breathing zone of worker, about 20-30 cm hemisphere around the nose and mouth (© Copyright 2018 SKC Inc.)

The sampling device includes a small light-weight pump which draws a known volume of air through a suitable sampling medium. After the measurement period, the sampling medium is then analyzed by an analytical laboratory. The analysis includes a determination of the chemicals captured in the medium, and where relevant, depending on the sampling head used, the particle size of the aerosol captured.

Further information on the personal sampling methodology to be applied is described in later sections of this guidance document.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

5. NUMBER OF PERSONAL EXPOSURE SAMPLES TO BE COLLECTED

Particular focus is given here to exposure assessment as required under REACH; however, it is also assumed that the collected data can also be used for checking compliance with respective OELs.

There is a need for as wide a range and number of Sb producer and downstream user sites as possible to participate in the campaign. As an absolute minimum at least two (ideally three) Sb producer companies and two (ideally three) per type of downstream user (flame retardant plastic; flame-retardant textile; PET catalysis; lead-acid batteries; glass and others where possible) should participate in the initiative. This minimum aims for:

(i) a good representability of the data: less extrapolations within and across production and use types require less assumptions and increases certainty and regulatory acceptability; and

(ii) a better opportunity for anonymization through aggregation, and the availability of sufficient exposure values to be used in the safety assessment or OEL determination (more sites = more values, and the smaller the assessment factors that are applied by authorities to cope with variability or small datasets).

It is acknowledged that those participating in the measurement campaign wish to have an understanding of the numbers of samples they may be required to collect at their site. This is no easy question to answer as it depends on a number of factors such as the numbers of exposed workers per site, work activities undertaken and how similar (or otherwise) these are in relation to activities taking place at other sites. A number of approaches can be used to determine sample size including guidance from ECHA (2016, 2014a) and BS EN 689:2018 which are briefly discussed below.

The ECHA Guidance on Information Requirements and Chemical Safety Assessment, Chapter R.14: Occupational exposure assessment (ECHA, 2016), gives advice to registrants on how to carry out an occupational exposure assessment and report safe use in the form of an Exposure Scenario (ES). This content can be used as starting point to determine the number of samples which need to be collected. Up until 2016, ECHA recommended collecting at least 6 samples to represent a single activity in one company and no less than 12 samples to represent the activity across companies in an industrial sector for the scenario being evaluated (ECHA, 2012a). This was based on the premise that it is unlikely that data for one company is representative of the entire industrial sector. Further, ECHA derived samples sizes based on the risk characterization ratio (hazard level divided by exposure level) and the uncertainty of the measured levels, which suggested that anywhere from between 6-12 to over 50 measurements may be necessary (Table 1). It should be highlighted that this table has since been removed from the more recent ECHA guidance (ECHA, 2016) but is provided here to provide context.

Table 1: Indicative number of measurements needed to determine confidently that the true Risk Characterization Ratio is below 1 (ECHA, 2012a)

		RCR: <1-0.5	RCR: <0.5-0.1	RCR: <0.1
		N	N	N
Variation and uncertainty in the data$	Low^	~20-30	12-20	6-12
	Moderate+	~30-50	~20-30	12-20
	High*	>50	~30-50	~20-30

N = number of samples
RCR = Risk Characterization Ratio
$ Variation and/or uncertainty can be caused by on the one hand true variation in exposure (as indicated by a measure of variation to be assessed. High: a high geometric standard deviation (GSD) in the measured data (e.g. > 3.5) or the representativeness of the variation) and on the other hand lack of knowledge about how representative the data are for the situ
* **High**: data is suspected to be significantly uncertain for the situation to be assessed.
+ **Moderate**: a moderate GSD (e.g. 2 – 3.5) and/or the representativeness of the data is questionable.
^ **Low:** a low GSD (e.g. < 2) and the data can be considered representative for the situation to be assessed

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

The ES defines the system of OCs, RMMs and PPE, which are applied during the manufacture and use of the substance during its lifecycle. This set of systems must ensure that all the human and environmental exposures arising from the handling, production or use of the substance are controlled. Therefore, the ES essentially profiles a 'safe ES' in terms of the conditions that ensure adequate control of risk to workers, consumers and the environment, when a substance is manufactured and used industrially, professionally or domestically, as appropriate (REACH 2006; ECHA, 2015; ECHA 2012b).

An ES can be made up of a number of sub-scenarios, referred to as contributing exposure scenarios (CES). These CES tend to differentiate the different parts of the ES based on exposure concentration levels, and are often linked with steps of the industrial process description. Different exposure concentration levels may arise at different points in the ES (as steps in the particular industrial process) due to the application of RMM or the plant design. The CES often represent i) (input) materials reception, ii) one or more processing/finishing steps, iii) packaging and iv) cleaning and maintenance.

Measurements can be pooled across different companies, who are part of same ES, and assigned to the appropriate CES. In this way, sufficient measurements, from which to derive an exposure estimate, can often be obtained. In automated processes, the number of employees working on a particular CES is often small. Sometimes sampling over successive shifts can help boost the number of measurements available to generate an exposure estimate. Alternatively, collecting good quality contextual data for the real-life work situation, which is representative of the CES, can reduce uncertainty in the exposure estimate by ensuring that the data adequately reflects the defined (C)ES. This is why it is also important that readers refer and follow the guidance provided in Part 2 of the monitoring guidance document. In addition, ECHA guidance recommends exposure estimation using exposure analogies (read-across) to fill these gaps (e.g. ECHA, 2016), which again requires the assessment of good quality contextual information.

Further guidance on how to define exposure groups and on the numbers of samples to be collected to compare the results with occupational exposure limit values (OELVs) can be found in BS EN 689:2018. In this, Similar Exposure Group (SEGs), are referred to. This is a group of workers having the same general exposure profile for the chemical agent(s) being studied because of the similarity and frequency of the tasks performed, the materials and processes with which they work, and the similarity of the way they perform the tasks. In essence, employees are placed into SEGs based on past monitoring data or via using the knowledge of persons working at the site as to the possible exposures. For each SEG, it states that a minimum number of samples is required, depending on the measured concentration. A preliminary screening test requires 3-5 valid exposure measurements for workers belonging to a SEG. If the results are all below:

- 0,1 OELV for a set of three exposure measurements, or
- 0,15 OELV for a set of four exposure measurements, or
- 0,2 OELV for a set of five exposure measurements,

then it is considered that the OELV is not exceeded and there is compliance. If one of the results is greater than the OELV, it is considered that the OELV is exceeded and there is non-compliance. If all the results are below the OELV and one result is above 0.1 OELV (set of three results) or 0.15 OELV (set of four results) or 0.2 OELV (set of five results) it is not possible to conclude on compliance with the OELV. In this situation, additional exposure measurements shall be carried out (requiring at least a total of six measurements).

Furthermore, a more general approach is taken by the American Industrial Hygiene Association (AIHA 1998, 2006) who suggest that 6-10 samples should be sufficient to give a picture of an exposure profile.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

Therefore, in summary, and also in the interests of efficiency with the measurement campaigns, during the first year of the campaign, it is recommended that 6 inhalable and 6 respirable samples per exposure situation should be collected in each company. If the number of measurements to be made is greater than the number of workers available, it will be necessary to measure some workers more than once. There may also be instances where due to time and budget considerations, it is not possible for a company to collect the required samples for each exposure situation present on their site. In this event, it is recommended that efforts are taken to identify the exposure situations where workers are exposed to the highest concentrations of Sb and sampling efforts be focussed on these. This practice should be informed, for example, by previous exposure measurement data and expert opinion. The criteria used to identify with certainty the exposure situations where the highest exposure concentrations can be expected must be objective, transparent, justified and documented.

However, it is upon the assessment of a given dataset of measurements collected in 2019 that the actual number of samples required during the 2020 measurement campaign (which can increase the dataset's ability to support a robust assessment) can be identified. Following 2020, an iterative/follow-up targeted monitoring campaign may be launched to collect missing exposure values afterwards if deemed necessary.

It is recommended that individual company specific discussions take place to finalize the site-specific monitoring and sampling strategy to be employed prior to the measurement campaign commencing.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

6. WHY THE NEED FOR A STANDARDISED SAMPLING APPROACH?

There are a number of methods available to sample both the inhalable and respirable dust fractions. Numerous studies have been published comparing the performance of different samplers, with IOM (2011) providing an overview of these. The results from these studies demonstrate that the use of different samplers can result in significant differences in the observed particle concentration. A number of factors have been identified which can affect the performance of samplers including inlet size, geometry, orientation, electrical charge, the sampler conductive properties amongst others (Aizenberg et al. 2001). 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.

As regards the chemical analysis of the sample, different methods (and specifics within these methods) may be considered. If one reference analytical approach is used, this reduces the risk of variability between samples, and maximises their comparability. Laboratories must ensure that the recommended method is implemented with the experience and care required to operate in full respect of the applicable laboratory practice and method.

The use of the same standardized methods to sample and analyse Sb in airborne particulate matter in the workplace atmosphere is therefore imperative and will ensure consistency in approach and allow pooling and aggregation of Sb exposure data across different Sb sites.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

7. DESCRIPTION OF THE SELECTED PERSONAL SAMPLERS

7.1 Introduction

For the purposes of the i2a measurement campaign, the concomitant use of two personal samplers are recommended in order to capture the inhalable and the respirable aerosols fractions.

- The IOM sampler has been shown to give the best agreement with the inhalable convention under the widest range of workplace conditions, and is the preferred method of sampling the inhalable aerosol. This sampler typically has a sampling bias of less than ±5% (HSE, 2014).
- The cyclone sampler of the generic Higgins Dewell type is recommended for optimal agreement with the respirable convention (HSE, 2014).

It is recognized that sites may already use other sampling heads to sample the inhalable and respirable samplers. No published studies have been identified that report comparisons of samplers used to determine the inhalable and respirable fractions for Sb. Development of a generic correction factor that may be applied to the measurement results obtained when using other inhalable and respirable samplers, relative to the IOM and Higgins Dewell cyclone sampling heads is therefore difficult. This is due to the different factors that influence sampling efficiency, particularly the differences in particle size distribution in different workplace environments, and would lead to a high level of uncertainty. A Sb specific sampler comparison study, which would consider all potential inhalable and respirable samplers that companies may already use, is not planned within the i2a measurement campaign due to time and budget constraints.

It should also be highlighted that the use of the IOM sampler with the multifoam disc, whereby the inhalable and respirable fractions are measured simultaneously within the same sampler, was investigated. Laboratory trials undertaken by IOM reported that the foam discs had a higher limit of detection and poorer recovery efficiencies than the filter sampling media, which would result in significantly longer sampling durations being necessary to be able to demonstrate compliance with the new German OEL is 0.006 mg respirable Sb/m3 for antimony trioxide and antimony trisulfide, for example.

It is therefore important that, for the purposes of the i2a campaign, inhalable and respirable samples are collected using the sampling methods described in this guidance document. Details of some suppliers of the IOM and Higgins Dewell cyclone sampling heads and indicative costs are provided in Appendix 1. In addition, many occupational hygiene consultants use these sampling heads and an option may be to approach them to discuss their assistance with the measurement campaign.

It should be highlighted that the sampling methods are recommended for use, irrespective of any respiratory protection being worn by the workers as the samplers should be placed external to those, and any other PPE being worn (thus uncovered).

7.2 IOM sampler

The IOM sampler is designed to collect inhalable particles (particles with an aerodynamic diameter below 100 µm collected with 50% efficiency) for optimal agreement with the CEN/ISO/ACGIH convention, when operated at 2.0 l/min (HSE, 2014). There are two versions of the sampler: one made of conductive plastic, and another of stainless steel. For personal sampling, the plastic head version is preferred as this is lighter and it is this version which is recommended.

The IOM sampler is composed of a sampling head and a filter cassette. The head comprises a cylindrical body, which will contain the reusable cassette, covered by a front plate. The cassette incorporates a 25-mm filter and a 15-mm circular inlet with a lip that protrudes 1.5-mm outwards (Figure 3). The purpose of the lip is to minimize the entry of particles deposited on the outer surfaces of the inlet into the sampler.

Figure 3. IOM conductive plastic sampler (Source: SKC. Inc)

Filters of mixed cellulose ester (25mm and pore size 0.8 µm) are considered to be the most suitable for sampling (and analysis) of total Sb, (as well as lead and arsenic for which laboratory analysis is also recommended) and should be used. If other types of filters are used, the Sb content in the blank filter should be lower than 0.1 µg per filter (ISO 15202, 2012). It should be highlighted that PVC filters should not be used due to an unstable solution being formed when these are prepared for analysis using microwave digestion.

.

7.3 Higgins-Dewell Cyclone sampler

The Higgins Dewell cyclone is designed to collect respirable particles (particles with an aerodynamic diameter smaller than 4 µm collected with 50% efficiency) for optimal agreement with the CEN/ISO/ACGIH convention, when operated at 2.2 l/min (HSE, 2014). There are two main Higgins Dewell cyclone manufacturers (SKC Ltd. and Casella Measurement); each offers a slightly different design. The SKC cyclone has the outlet at the top of the cyclone, whereas the Casella cyclone has the outlet on one side (Figure 4). The cyclone is available in conductive plastic and metal. For personal sampling, the plastic version is preferred as this is lighter than the metal cyclone.

It is important to highlight that SKC recently communicated that the SKC plastic Higgins-Dewell style cyclone (model number 225-69) may oversample[6]. To verify the degree of any oversampling, SKC arranged for the SKC plastic cyclone to be assessed against BS EN 481 at the current flow rate of 2.2L/min. This confirmed that at this flow rate the SKC plastic cyclone can oversample by up to 30%. However further testing at various different flow rates confirmed that if used at a flow rate of 3.0 l/min the performance conforms extremely well to the respirable convention.

[6] http://weber.hu/Downloads/SKC/SKC_PlasticCyclone225_69.pdf

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

Figure 4. Higgins Dewell cyclone sampler (SKC on right, Casella on left)

The rapid circulation of air separates particles according to their aerodynamic diameter. Particles larger than 4 µm are forced to the periphery of the air stream, falling into a grit pot and are discarded (Figure 2). Particles of a diameter below 4 µm remain in the center 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.

Filters of mixed cellulose ester (25mm and pore size 0.8 µm) are considered to be the most suitable for sampling (and analysis) of total Sb, (as well as lead and arsenic for which laboratory analysis is also recommended) and should be used. If other types of filters are used, the Sb content in the blank filter should be lower than 0.1 µg per filter (ISO 15202, 2012). It should be highlighted that PVC filters should not be used due to an unstable solution being formed when these are prepared for analysis using microwave digestion.

.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

8. REQUIRED EQUIPMENT AND MATERIALS FOR SAMPLING

Below is a list with the equipment and materials needed for performing air measurements for both the inhalable and respirable size fractions. It is recommended that assembled IOM cassettes and cyclone cassettes (preloaded with pre-weighed 25 mm filters) are provided by the laboratory which will be used to analyse the collected samples.

- IOM inhalable sampler, in conductive plastic (e.g. SKC 225-70A)
- IOM-cassettes (25 mm), in conductive plastic, with transport clip and cover (e.g. SKC 225-71A)
- Higgins Dewell cyclone, in conductive plastic
- Cyclone cassettes (25 mm), in conductive plastic, with metal support grid and transport clip (e.g. SKC 225-62)
- Spare O-rings for sampling heads (IOM, pack of 4 P22570)
- Filters of mixed cellulose ester (25mm and pore size 0.8 µm) - these must be identified with unique sample identification codes, with these codes being used to identify the samples during all measurement, analysis and reporting stages.
- High flow air pump, capable of operating for up to 8 hours at a flow rate of 2 L/min (inhalable dust fraction) or 2.2 L/min or 3.0 L/min (respirable dust fraction, depending on Higgins-Dewell sampling head used), with battery charger, e.g. Gilian GilAir-5 pump (Sensidyne), AirCheck 52 pump (SKC 224-52), Sidekick pump (SKC 224-52MTX), Buck Genie VSS-5. Please note that if sampling is to be undertaken in explosive environments (can be caused by flammable gases, mists or vapours or by combustible dusts) certified intrinsically safe pumps must be used to minimize the risk of ignition and explosion.
- Flow rate calibrator, e.g. Defender 510 (BIOS DryCal), TSI Mass flow meter 4140, calibrated against a primary standard, capable of measuring the required flow rates
- IOM calibration adapter (e.g. SKC 391-01)
- Screw drivers to adjust flow rate, where needed
- Protective pump pouches (e.g. SKC 224-88 for Sidekick pump) and belts / harnesses to allow sampling equipment to be attached to wearer
- Supply of clips to attach sampling heads to participants (if not already on sampling head)
- Sufficient lengths of flexible tubing of suitable diameter for making a leak proof connection from the sampling head to the pump
- Calibrated timepiece
- Powder free disposable gloves
- Sample record sheets
- Pens

It is recommended that a suitable, specific risk assessment is undertaken prior to performing the measurement campaign, to ensure that the health and safety of the workers to be involved is not at increased risk due to the wearing of the sampling devices.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

9. OVERVIEW OF SAMPLING ACTIVITIES

Figure 5 provides an overview of the key activities to be undertaken before, during and after sampling.

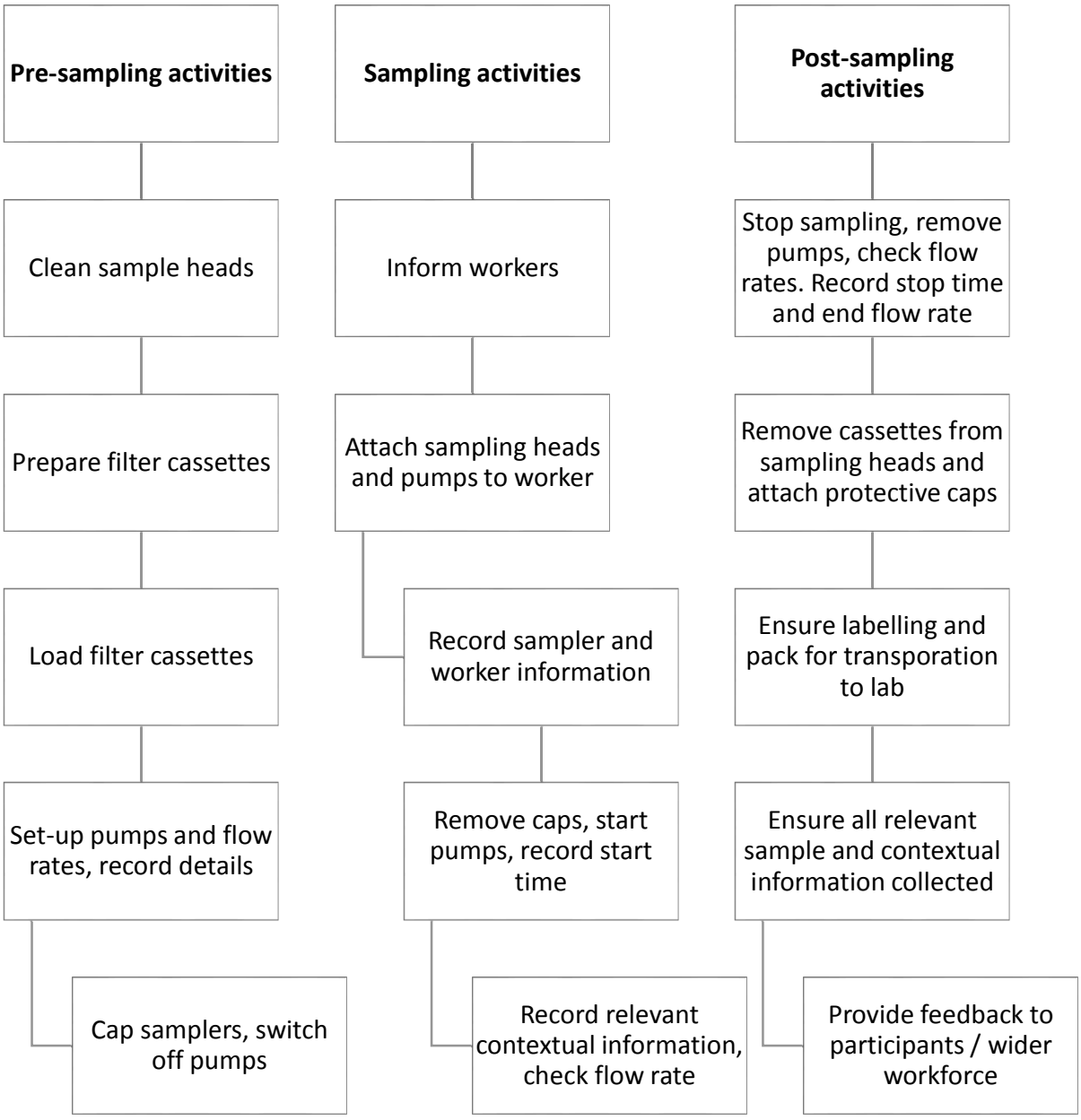

Figure 5. Overview of key activities undertaken before, during and after sampling

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

10. PRE-SAMPLING ACTIVITIES

These should all be undertaken in an uncontaminated area.

10.1 Cleaning

All samplers' components should be cleaned prior to any sampling. Samplers should also be checked for defects before use. Exploded diagrams of the two samplers to illustrate the different components are shown in Figures 6 and 7, for the IOM and cyclone samplers respectively.

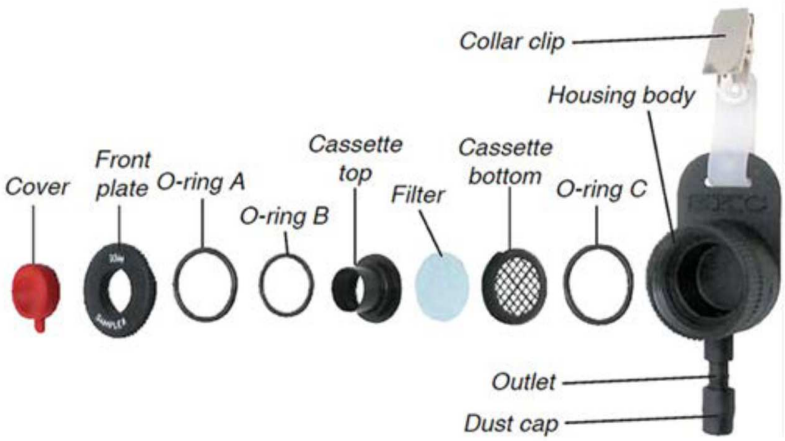

Figure 6. Conductive plastic IOM sampling head and cassette (Source: http://www.skcinc.com/prod/225-70.asp)

Figure 7. Casella (left) and SKC Ltd. (right) cyclones components

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

Cleaning is performed after all sampler parts have been disassembled. Cleaning can be done by soaking all the sampler's parts in a mild soap solution, rinsing thoroughly with clean water and air-drying. An ultrasonic cleaner may be used but is not essential.

The IOM sampler O-rings (A, B and C) (Figure 6) should be cleaned separately using water only. The purchasing of extra O-rings is recommended in case they are misplaced/damaged during assembly and disassembly.

If the samplers are used repeatedly on the same day of sampling, after each sampling period, the samplers should be cleaned with a lint-free cloth to eliminate any residual dust. The grit pot of the cyclone should be cleaned between surveys using a lint-free cloth or brush.

Allow components to dry (in a clean, contaminant free environment) before assembly, weighing, and use.

10.2 Preparing the filters / cassettes

Wherever possible, it is recommended that the analytical laboratory provide the pre-weighed filters, pre-loaded in the IOM / cyclone cassettes, so that these are ready for loading into the cleaned samplers. These filters should be identified with a unique sample identification code, with this code being used to identify the sample during all measurement, analysis and reporting stages.

Information on weighing the filter / filter cassettes is available on MDHS 14/4 (HSE, 2014) and as such is not duplicated here. Should site personnel responsible for the measurement campaigns be required to load the weighed filters into the cassettes, the procedures for doing so are outlined in the following sections.

10.3 Loading IOM cassettes

Figure 8 illustrates the first two steps (after weighing the filter and before weighing the cassette containing the filter) required to assemble the IOM sampler: Place the filter on the cassette bottom using clean (flat tipped) tweezers. Then snap the cassette top onto the cassette bottom containing the filter, ensuring a tight fit (and weigh the filter and the cassette).

Step 1 **Step 2**

Figure 8. Loading of filter in the IOM cassette

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

If not sampling immediately or if transporting pre-weighed loaded cassettes to a sampling location, the cassette containing the filter should be covered with an IOM protective cover (to prevent dust from entering the sampler when transporting the cassette). The covered cassette is placed in a transport clip (Figure 9). Each cassette must be identified with a unique sample identification code, with this code being used to identify the sample during all measurement, analysis and reporting stages.

Figure 9. Loaded cassette with IOM cover awaiting to be labelled and used for sampling

10.4 Loading cyclone cassettes

Insert the filter support grid on the cassette top and place the filter over the grid (Figure 10). Snap the top of the cassette onto the cassette bottom and make sure it is tight (and weigh the cassette).

When not ready to sample immediately or when transporting pre-weighed loaded cassettes to a sampling location, the cassette containing the filter should be closed with a transport clip (Figure 7). Each cassette must be identified with a unique sample identification code, with this code being used to identify the sample during all measurement, analysis and reporting stages.

.

Step 1 **Step 2**

Figure 10. SKC Ltd. cyclone filter assembly

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

10.5 Loading cassettes into IOM sampling head

- Wear powder free disposable gloves when handling the sample cassettes.
- Remove IOM cassette (pre-loaded with pre-weighed filter) from its transport clip and remove the red protective cap.
- Unscrew the top plate from IOM sampling head housing body. Ensure the O-rings are positioned correctly (Figure 11).
- Insert the IOM cassette into the IOM housing body. Screw the top plate into the housing body. Tighten securely to achieve a good seal. (Figure 12).
- Place a label with the unique sample identification code securely on the back of the sampling head.

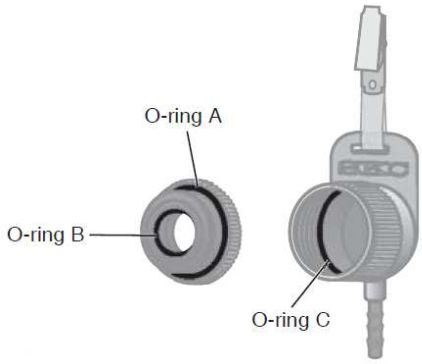

Figure 11. O-ring placement for plastic IOM sampler

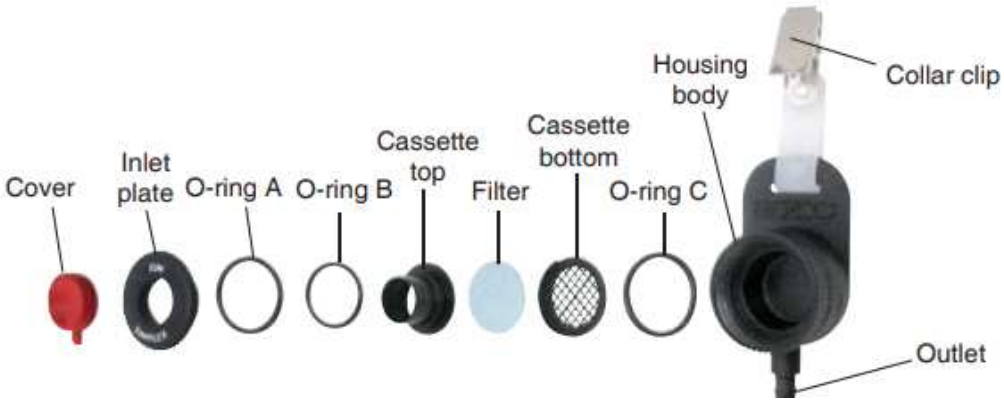

Figure 12. Configuration for plastic IOM sampler and cassette

10.6 Loading cassettes into cyclone sampling head

- Wear powder free disposable gloves when handling the sample cassettes.
- Remove cyclone cassette (which contains the filter) from its sealing clip.
- Unscrew the cyclone sampler top from the sampler body. Ensure the O-rings are positioned correctly (Figure 13).

- Fit the cyclone cassette (with the filter inside) into the cyclone sampler body with the cassette top upwards (the filter should be facing down, towards the air inlet). Screw the sampler top into the sampler body. Tighten securely to achieve a good seal. Ensure that the clean and empty grit pot is securely fitted over the ridge around the bottom of the sampler body (Figure 13).
- Place a label with the unique sample identification code securely on the back of the sampling head.

Figure 13. Configuration for plastic cyclone sampler and cassette

10.7 Set-up of pumps for sample collection

Personal sampling pumps will be used to draw air through the personal samplers worn by the workers. Note - if sampling is to be undertaken in explosive environments, certified intrinsically safe pumps must be used.

Personal sampling pumps that meet the requirements of BS EN ISO 1313712 should be operated according to the manufacturer's instructions. Sampling pumps should have the following features as a minimum:

- an automatic flow control which keeps the volumetric flow rate within ±0.1 l/min in case of changing back pressure caused by filter loading;

- either a malfunction indicator, which following the completion of sampling, indicates that the air flow has been reduced or interrupted during sampling, or an automatic cut-out, which stops the pump flow if it is reduced or interrupted;
- a facility for adjustment of the flow rate that prevents inadvertent adjustment during use;
- pulsation damped flow for cyclone samplers.

A calibrated flow meter will be necessary to set and check the samples to the required flow rate (Figure 14).

Figure 14. Examples of flow meters

The calibration of the flowmeter shall be checked against a primary standard, i.e. a flowmeter whose accuracy is traceable to national standards. If appropriate, it should also record the atmospheric temperature and pressure at which the calibration of the flowmeter was checked.

It is advisable that the flowmeter used is capable of measuring the volumetric flow rate to within ± 2 % or better.

Flexible plastic tubing, with a suitable diameter for making a leak proof connection from the sampling head to the pump, should be used. This should be of sufficient length to ensure that the pump can be worn on a belt or harness, sampling head located in the breathing zone, without the workers movement being impeded.

Before attaching the samplers to the workers there is need to perform a leak test and set the sampler to the required flow rate.

Remove any protective cover or cap from the sampler, switch on the sampling pump and allow the pump flow to stabilise according to the manufacturers.

Switch on the pump and allow the flow to stabilise for a few minutes. Attach the calibrated flow meter to the inlet of the sampler (using an adaptor if required) so that it measures the flow through the inlet. Set the flow rate of the sampler to within ±0.1 L/min of the prescribed flow rate:

- 2.0 L/min for IOM sampler
- 2.2 L/min for Casella Higgins Dewell cyclone sampler
- 3.0 L/min for SKC Model 225-69 Higgins Dewell cyclone sampler

It is recommended that three separate flow rate measurements are collected so that an average can be obtained. The flow meter should then be disconnected.

Details of the sample and pump numbers, as well as the set flow rate should be recorded on the sample record sheet (available in Part 2 of the Monitoring Guidance document).

Perform a leak test by covering the sampler's inlet and / or 'kinking' its tube. The frequency of the pump should increase, the flow rate decrease, and the pump should stop pumping. If this happens, the sampler was properly assembled and can operate according to the flow rate foreseen. If this does not happen, the sampler was not properly assembled and should be disassembled and re-assembled, and the leak test performed again.

Once the checks are completed, switch off the pump and recap the sampler.

If the temperature, humidity and pressure in the environment where the samplers are to be used differ significantly from where the flow rate was set, the volumetric flow rate may change and may need to be readjusted just before sampling.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

11. SAMPLE COLLECTION

This section is divided into three parts, these being:

1. Activities before and at start of sampling period, which includes placement of samplers on participants and starting the pumped sampling;
2. Activities at start and during the sampling period, which includes the contextual information to be recorded during sampling; and
3. Activities at the end of the sampling period, including removal of the sampling heads and preparing samples for transportation to the analytical laboratory.

Prior to discussing these three elements to sample collection, the duration of sampling is discussed.

11.1 Sample duration

Sample duration is an important factor that can influence the representativeness of exposure measurements. The sampling duration should be chosen to represent the exposure for the exposure scenario and describe the exposure for the reference period being assessed (BS EN 689:2018).

For example, to demonstrate compliance with an 8-hr time weighted average (TWA) OEL and if the workplace factors are constant during the whole shift, it is recommended by BS EN 689 that the total sampling duration should be a minimum of 2 hours if the sampling period can be considered to be representative of the work shift. The Standard further states that, in order of priority, measurements should be collected for the full shift, for one exposure period of at least 2 hours, with the final option being to measure for more than one period of exposure (i.e. two periods of 1 hour). However, it is considered good practice to sample for at least 75% of the full shift.

BS EN 689 also recommends three options for instances when workplace factors are not constant during the shift, and exposure only occurs part of the shift. These are:

- measuring for the full shift and using the average exposure for the whole shift;
- measuring for the total period of exposure and assuming that the exposure for the rest of the shift is zero after careful examination to calculate the 8-hr TWA; and finally
- measurement of the period of highest exposure and assuming this applies to the total period of exposure.

In the situation whereby workplace factors are not constant during the shift and there are multiple ES during the whole shift and tasks are randomly distributed during the work shift, the sampling duration should correspond to the shift duration. For this, BS EN 689 recommends two alternative approaches:

- to measure for the full shift; or
- that each task is measured separately and that these results are then used to calculate an average exposure over the whole shift.

Finally, in instances where a single exposure situation is repeated a number of times during the whole shift, BS EN 689 recommends three alternatives:

- measure for the full shift and use the average over the shift;
- measure for at least one cycle of the exposure profile or, if a cycle lasts less than 2 hours, for at least 2 hours and for a complete number of cycle; and
- measure for the period of highest exposure, which is then assumed to apply for the period of exposure.

Overall, it is recommended that, when comparing against an 8-hr TWA, the sample duration is for a representative period of the workers shift (>75% of the shift, excluding their lunch break). It is likely that in some companies there are activities involving Sb substances for only a very short time every day and that for the remaining time activities are undertaken where there is no exposure to Sb. In situations where these activities have been clearly defined, that it is possible to distinguish clearly between the times during which there is exposure to Sb and times when

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

there is not, and this is supported by previous good quality exposure measurements, it is possible to monitor only for the period for which exposure occurs. However, to demonstrate compliance with the new German OEL of 0.006 mg respirable Sb/m^3, this would require the ability to report down to 10% of this value (0.0006 mg or 0.6 µg). It is therefore important to also consider the analytical reporting limit for Sb for the company's assigned laboratory, as well as the exposure situation when determining the minimum sample duration.

The minimum sample volume to determine compliance with the OEL can be calculated using Equation 1:

*Equation 1: Sample volume (L) = LOD (µg) / exposure limit (*mg/m^3)*

* note that the exposure limit here is a 1/10th of the German OEL (0.006 mg/m^3)

For example, assuming that the assigned laboratory has a reporting limit of 0,025 µg Sb /filter, we calculate the required minimum sample volume as follows:

Sample Vol (L) = LOD (µg) / Exposure limit (mg/m^3)* = 0.025/0.0006 = 41.67 L

This would mean that when using the cyclone sampling head, a minimum sample duration of 20 minutes would be required (41.67 L being divided by the flow rate of the cyclone sampler, this being 2.2 l/min) and for the IOM sampling head, the minimum duration would be 21 minutes).

It is recommended that individual company specific discussions take place to discuss the assigned laboratories analytical reporting limits and proposed sampling durations prior to the measurement campaign commencing.

11.2 Start of sampling period

Prior to their participation in the measurement campaign, employees should be provided with an explanation of the campaign's objectives and the importance of their participation. Employees should be advised to ensure that they do not cover the sampling heads, e.g. when donning, and if closing, jackets. They should also be asked to inform the researcher as soon as possible if they notice anything strange with the pump (e.g. stops making a noise or flashes a different colour / stops flashing) or the tubing becomes detached. Employees being sampled should be reminded to carry out their work duties and tasks as normally as possible. In addition, employees should be advised that the occupational hygienist responsible for the monitoring will periodically be working in and around their workplace to observe their activities and to check that the samplers are working correctly.

Sampling simultaneously with the IOM and the cyclone samplers requires the employee to wear two pumps. Both sampling heads should be positioned on the dominant side[7] of the worker, taking care to ensure that they do not block the airflow of the other. Employees should be informed of this, and the occupational hygienist must ensure that the weight of the two pumps does not interfere with the employee's working tasks. Care should be taken to ensure that neither the position of the pumps, nor tubing interferes with the workers' range of movement.

The following steps should be taken to place the samplers on the employee and start the personal sampler:

- Employees should be given a belt or harness to wear and carry the necessary sampling equipment. Care should be taken to ensure that neither the pumps, nor the tubing impede the workers' ability to work.
- Attach both pumps to the worker's belt or harnesses so that they cause minimum inconvenience to the worker and safely secure the pump tubing.

[7] E.g. If the worker is right handed, samplers should both be located on the right-hand side of the workers breathing zone

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

- Attach both samplers to the worker's upper chest or lapel using the collar clips, preferably on the workers dominant side. Samplers should be placed in the breathing zone, not more than 30 cm away from the nose-mouth region (see Figure 2).
- Record name and job title of employee next to the sample numbers on the sample record sheet (available in Part 2 of the Monitoring Guidance document). Note – names are recorded to help with sample tracking during the measurement period but are not used for reporting.
- Make sure the air intake opening of the IOM cassette is pointing outwards (not upwards or down).
- Cyclone sampler should be attached with the grit pot pointing downwards (see Figure 3).
- When ready to begin sampling, remove protective cap from the IOM sampler.
- Switch on the two pumps and record the time on the record sheet (available in Part 2 of the Monitoring Guidance document), using a calibrated timepiece.
- Employees should again be instructed not to touch or cover the samplers and that the occupational hygienist will check in with them again at a suitable time to ensure that the pumps are working correctly.

11.3 During sample period

An Excel template has been developed for use when carrying out the monitoring campaign at the participating sites. This is to record all relevant information and observations made during the measurement period and also general background information that will inform the findings from the monitoring campaign. The use of this template ensures that all sample and contextual information is collected in a consistent manner across all participating sites and it is recommended that all notes taken during the sampling campaign be recorded in the designated i2a template file. The template and details on how to complete this is provided in Part B of this Monitoring Guidance document.

Details of the types of contextual information that will be gathered includes, but is not limited to, the following:

- assigned (C)ES codes
- location (indoors and outdoors)
- production and work scheduling - production hours (24/7 or otherwise), shift system, number of workers per shift/team
- range of Sb products made /used by the company
- operational conditions (temperature) for plant and equipment used
- routine and non-routine tasks by work pattern (frequency and duration) and work practices (task description)
- process classification (continuous / batch) across operations and tasks
- level of automation, mechanization and manual interventions in process
- all RMM employed, e.g. use of enclosures, separation of workers from emissions, local exhaust and general ventilation, personal protective equipment (PPE) worn

A separate guidance document will provide companies with detailed information on how to complete the designated templates.

In addition, during the measurement period, the following should be undertaken with respect to the sampling equipment being worn by the workers:

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

- The sampling equipment should be checked within the first hour of sampling. If the sampling duration extends over a number of hours, the correct functioning should be checked every 2-3 hours. Similarly, the flow rates should be assessed at regular intervals (every 2-3 hours) until the conclusion of the sampling period, as well as at the end of the sampling period.
- Air sampling should be interrupted during lunch breaks and pumps should be switched off and removed from the worker during this time. If it is possible to remove the pumps from the worker during any shorter refreshment / rest periods that they may have, then this is encouraged. However, it is accepted that this may not always be possible, and in such instances a record should be made of the duration of time that the pumps are worn by workers during break times.
- Flow rates should be checked during lunch breaks (and other beaks if possible), being adjusted as necessary. If the flow rate has deviated by greater than 0.1 l/min then the sample should be considered void and should be removed and discarded.
- Record the time that the pumps were switched off and then back on during the lunch period and also the flow rates at each point on the sample record sheet.

11.4 End of sampling period

The following steps should be taken to remove the samplers from the employee, measure the final flow rate, stop the personal sampling survey, and carry out calculations of sample volume:

- During all stages detailed below, take care to minimize mechanical shock which could result in the sample becoming dislodged/disturbed from the filters.
- Help remove the pumps (while it is still running/switched on) and sampling heads from the worker.
- Measure and record the flow rate on the sample record sheet (available in Part 2 of the Monitoring Guidance document).
- Switch off the pumps and record the time on the samples record sheet, using a calibrated timepiece (available in Part 2 of the Monitoring Guidance document).
- Carefully disconnect the samplers from the tubing.
- Cyclones must be always retained upright to avoid contents of the grit pot falling onto the filter.
- Remove the IOM cassette from the IOM sampler and attach the protective cap on the IOM cassette and fasten with transport clip. Alternatively, it may be practical to cap the IOM sampler and return to the laboratory for disassembly.
- Remove cyclone cassette and fit the sealing clip over the cassette.
- Ensure that all cassettes are still labelled correctly and place in zip lock bags.
- Calculate the average flow rate at the beginning and at the end of the measurement. If the two flow rates differ by more than 5%, consider the air sample as invalid.
- Calculate the sampled air volume by using the following equation (Equation 2):

Equation 2: Volume of air sampled (m^3) = Sample flow rate (l/min) x sample time (mins)

Example: Flow rate = 2.00 l/min
Sample time = 8 hours = 8 x 60 = 480 minutes
Volume of air = 2 (l/min) x 480 (minutes) = 960 litres
Volume of air = 960 / 1000 = 0.96 m^3 (cubic metres)

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

- Transport samples to the selected analytical laboratory, providing details of the relevant sampled air volume for each sample number.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

12. QUALITY CONTROL / ASSURANCE AND FIELD BLANKS

For quality assurance purposes, field blanks must be obtained with each sampling survey. Field blanks are filters handled in an identical manner to the exposed filters (inserted in the cassettes, conditioned and weighed and taken to the field as exposed samples) with the exception that no air will be drawn through them.

One field (site) blank is required for every ten of each type of sample collected, with a minimum of three blanks for each batch of sample type. Field blanks are used to correct for any weight changes caused by atmospheric conditions and the handling of the media during sampling. For this reason, it is essential that field blanks are exposed to the same conditions as the samples apart from the period of sampling and not being worn by the worker. Details of the environmental conditions at the time of sampling (e.g. air temperature, relative humidity) should also be recorded.

Filter blanks should be collected separately for inhalable and respirable samples.

In addition to field blanks, the analyst has the option of preparing laboratory blanks which may be used to assess the weighing precision.

It is important to highlight that there are various factors that may affect the validity of the collected aerosol sample, such as:

- Presence of projectile particles (e.g. metal fragments from grinding processes) or splashes (e.g. mineral oil) entering the sampler;
- Large particles entering the sampler that are outside the inhalable definition (i.e. particles with aerodynamic diameters greater than 100 µm); and/or
- Transportation losses (e.g. particles falling off the filter) (HSE, 2014).

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

13. LABORATORY ANALYSIS OF COLLECTED SAMPLES

13.2 Introduction

The cassettes (fitted with the transportation clips) need to be sent to an analytical laboratory to allow the Sb concentration to be determined. i2a also requests that the collected filters are analyzed for lead (Pb) and arsenic (As), as these are known impurities which may contribute to the overall health condition of workers.

As with sampling, uncertainty in the measurement results can occur due to differences in analytical methods being used and / or different laboratories undertaking the analysis. For examples, such differences have been observed in the analysis of other agents such as oil mist and vapour (e.g. Galea et al., 2012). Confidence in the analytical result is increased when laboratories are independent of the company for which the samples were collected and where they able to demonstrate competence in the analytical methodology to be employed, e.g. through participation on a inter laboratory comparison (or proficiency test or PTP or round robin test) which consists of testing the same samples by different laboratories and in comparing the results. However, no existing proficiency scheme with respect to the analysis of workplace air samples for Sb was identified and it is therefore required that a standard methodological approach is adopted.

13.2 Proposed methods

When selecting an analytical method for which to analyze the collected samples due consideration needs to be given to the following:

1. Depending on the characteristics of materials being manufactured and used at the participating companies, a range of antimony compounds may be present, which have different solubilities. Therefore, to allow for total Sb to be determined, the analytical method requires an extraction method which is believed to be suitable for all compounds.
2. In addition, i2a requests that the samples are also analyzed for As and Pb, therefore the analytical method should be suitable for these agents too.

On behalf of i2a, VITO completed a Sb-specific laboratory validation exercise (Tirez et al, 2019), with the outcomes of this exercise recommending that the following ISO standard are applied for the sample preparation and analysis of the collected samples:

- Sample preparation: ISO 15202-2 Workplace air -- Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry -- Part 2: Sample preparation (Annex G) (ISO, 2012b)
- Analysis: ISO 30011:2010 F Workplace air -- Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma mass spectrometry (ISO, 2010).

Annex G of ISO (2012b) specifies a method for the dissolution of metals and metalloids and their compounds in a closed vessel microwave dissolution system using nitric acid (HNO_3) and hydrofluoric (HF) acid. To facilitate sample dissolution of certain metals and metalloids, e.g. Sb, it is also mentioned to additionally use hydrochloric acid (HCl). The use of HF acid is only mandatory when silicates are present in particulate matter to break up the silica matrix and to dissolve mineral constituents. Due to the corrosive characteristics of this acid, it has to be handled with special care. For this reason, there is a tendency to use HBF_4 instead of HF in dissolution methods of metals and their compounds metalloids (in silicate matrix). In short, a sampled filter + 4 ml HNO_3 + 1 ml HCL + 1 ml HBF_4 is placed in a microwave vessel. Subsequently, the temperature is raised to 180°C in 25 minutes and hold at an operating temperature of for a further 25 minutes.

Commonly, elemental analysis of airborne particulate matter is carried out by means of Inductively Coupled Plasma Mass Spectrometry (ICP-MS) or Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES). For the determination of Sb, analysis by quadrupole ICP-MS is advantageous when compared to methods such as ICP-OES, due to its sensitivity and the presence of fewer spectral interferences. It is however acknowledged that it is more costly when analysing samples by this method.

This selection of ISO standard methods was found to be fit-for-purpose by VITO for the determination of antimony in airborne particulate matter in the workplace atmospheres and the validation data, derived from two industrial workplace atmospheres, cope with the performance criteria stipulated in ISO.

i2a recommends that these ISO methods are applied and laboratories undertaking the sample preparation and analysis should follow the procedures specified in these methods. If the assigned laboratories do not already have copies of these available, they can be purchased at the on-line ISO store, https://www.iso.org/store.html.

13.3 Analytical laboratories

It is not possible to provide a comprehensive list of European analytical laboratories who have demonstrated capabilities in undertaking the requested laboratory analysis. It is recommended that any analytical laboratory used must work according to the ISO standards, good laboratory practice, adopting the following quality control and assurance methods, confirming that these were in place:

- Recovery checks – For every batch analyzed, a recovery sample is prepared by spiking known quantities of antimony onto a filter, and prepared alongside the samples.
- Quality control (QC) calibration standard – A separate QC sample is prepared with every batch of samples, to validate the calibration curve. Results must be within 10% of the expected level.
- Sample repeats – One in every 10 samples analyzed is repeated (e.g. sample is either halved prior to analysis or once the sample has been digested and made up to volume, the resulting solution is split into two separate sample containers. This repeat must be within 10% of the original.
- Standard repeat – As a minimum, a standard is re run after every tenth sample, results must be within 10% of the original result.

Confirmation that these requirements have been met must be detailed in the supporting contextual information records to be supplied for inclusion in the central data repository.

It is important to ask the analytical laboratory what their Limit of Detection (LOD) and Limit of Quantification (LOQ) is for the analysis and how this was defined[8]. This is important in determining the minimum sample duration to detect to 1/10th of the new German OEL (see Section 11.1).

[8] Limit of detection (LoD) – the smallest amount or concentration of analyte in the test sample that can be reliably distinguished from zero. Limit of quantitation (LoQ) – the lowest concentration at which the analyte can not only be reliably detected but at which some predefined goals for bias and imprecision are met. The LoQ may be equivalent to the LoD or it could be at a much higher concentration.

14. DATA REPORTING, SUBMISSION AND ANALYSIS

The inhalable and respirable sample data generated by the analytical laboratory and the supporting contextual information collected during the sampling is to be returned to the IOM using the specified templates. Guidance on the completion and return of these is provided in Part 2 of this Monitoring Guidance document and so the contents of this are not duplicated here.

It is requested that the results for the measurement period that the sample was collected are provided. In addition, companies or their consultants may also calculate the 8-hr TWA, which is represented mathematically by Equation 3 (HSE, 2018):

Equation 3: $(C_1T_1+C_2T_2+\ldots C_iT_i+\ldots C_nT_n) / 8 =$ *8-hour TWA concentration*

where C_i is the exposure concentration and T_i is the associated exposure time in hours. HSE (2018) provides further information on how such calculations are undertaken.

In instances where the 8-hr TWA are calculated, these results should also be provided. It should be highlighted that the measurement results should not be adjusted to reflect any RPE being worn.

Upon receipt by the IOM, the supplied data will be assessed against the following assessment criteria, for inclusion within the overall Exposure Monitoring campaign database:

- Sampler used: Sampling was carried out in accordance with i2a's Guidance Monitoring.
- Sample analysis: Analysis was performed in accordance with i2a's Guidance Monitoring.
- Sample result: Sb, Pb and As analysis results (and unit of measurement) are provided.
- Contextual information: Result has required contextual information (e.g. specific workplace, process, task, description of the operational conditions, risk management measures in place).

Samples not fulfilling these basic criteria will not be included in the exposure database (may potentially be considered for qualitative assessment only).

The exposure measurement results will be converted to a common unit. Measurement results that were identified as being less than the limit of detection (LOD) were assigned a value of half the LOD where this was provided. A simple descriptive analysis (number of measurements, mean (AM), standard deviation (SD), geometric mean (GM), geometric standard deviation (GSD), minimum (min), maximum (max) and 75, 90 and 95th percentile (where more than 6 measurements were available) of the pooled collected inhalable and respirable data will be completed for each identified SEG, CS, and Sb substance and presented in a report outlining the results of each phase of the measurement campaigns. Summary information for the Pb and As measurement results will also be provided.

An example of how the summary statistics will be presented is provided below (Table 2), with no site / company being explicitly named as contributing to the data summarized in tables within the report.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

Table 2: Example summary inhalable and respirable statistics for Antimony metal, ES9.1: Manufacture - Use of antimony containing materials in the recycling/production of antimony metal, CES Raw material handling for Sb (mg/m3)

Aerosol Fraction	Sites	No. results	No. results <LOD	AM	SD	GM	GSD	Min	Max	75% ile	90% ile	95% ile
Inhalable												
Respirable												

Whilst IOM are responsible for the collation of the provided exposure and contextual data and the analysis of this to provide the summary statistics, i2a will be provided with a copy of the overall exposure database which does not include company names. IOM will retain and share with EBRC (subject to appropriate confidentiality agreements) a version of the database where the company names remain linked with the data that they provided to assist with linkages with other previous data collection initiatives under REACH.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

15. PARTICIPANT AND COMPANY FEEDBACK

To ensure continued engagement by workers in this, and any other occupational hygiene measurement campaigns, it is important to provide timely feedback on the results and any actions being implemented in response to these in a timely manner.

It is therefore strongly recommended that upon receipt of the measurement results that workers are provided details of their results and how these compare with current OELs in place. Workers should be informed whether there is a need for changes in the RMMs and provided with necessary information, training and instruction with respect to these.

It is also recommended that the wider workforce are provided summaries of the results from the companies monitoring campaign, as well as details of the results from the overall monitoring campaigns.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

16. OCCUPATIONAL HYGIENE RESOURCES AND YOUTUBE VIDEOS

Further freely available information on the basic principles in occupational hygiene and the measurement of hazardous substances can be found at the following links.

http://www.ohlearning.com/training/training-materials/w201-basic-principles-in-occupational-hygiene.aspx

http://www.ohlearning.com/training/training-materials/w501-measurement-of-hazardous-substances.aspx

There are also a number of freely available YouTube videos on-line which, whilst not specifically related to personal sampling for Sb, can provide useful additional visual information and guidance on the collection of inhalable and respirable samples for the purposes of this measurement campaign. Some suggested links are provided below. Note that i2a accepts no responsibility for the content of the YouTube videos. Also, there may be some differences in practice to what is recommended in this guidance - in such cases, contents of this guidance document prevail.

16.1 Occupational Hygiene

What is occupational hygiene - https://www.youtube.com/watch?v=VlsLoqtep6k. Published on 11 Nov 2013. "This video outlines some of the different hazards Occupational Hygiene entails".

Module 1: Occupational hygiene principles. https://www.youtube.com/watch?v=NsVnEFVYiik. Published on 6 Nov 2014. "The objectives for this module are that, by the end, learners should be able to (1) classify the types of hazards workers face, (2) define "exposure" and related terms, (3) list the routes by which workers can be exposed to hazardous agents, and (4) describe the occupational hygiene framework of anticipating, recognizing, evaluating, and controlling workplace hazards".

Industrial hygiene sampling strategy - https://www.youtube.com/watch?v=bdkdsV-fFNM. Published on 2 Feb 2018. "Industrial hygiene sampling strategy, monitoring plan and exposure assessment models".

16.2 Air sampling

Introduction to air sampling - https://www.youtube.com/watch?v=UuD6RUUID48. Published on 6 Sep 2013. "A basic introduction into the types of air sampling for occupational exposures to hazardous substances and chemicals".

SKC basic air sampling - https://www.youtube.com/watch?v=6I7F9tCxUK0. Published on 29 Apr 2010. Learn why you need to perform air sampling and how to take air samples using a filter cassette, a sorbent tube, and a passive sampler

Personal air sampling - https://www.youtube.com/watch?v=u7gKsfvLt4U. Published on 6 Sep 2013. "An introduction into the types of air sampling that can be performed on an individual person. Personal sampling is used to determine the actual amount of exposure that person has had to a hazardous chemical, substance, or particles".

16.3 Inhalable sampling using IOM sampling head

Assembling the IOM - https://www.youtube.com/watch?v=BEV0boB-RRc. Published on 6 May 2014. "This is a quick overview of the IOM parts and how to assemble them with MCE filters".

IH Sampling for Inhalable Particulate Using IOM Samplers - https://www.youtube.com/watch?v=mgPC0JzLRIg Published on 29 May 2017. "When collecting air samples for inhalable dust while using IOM samplers, this short video from Maxxam will assist you in achieving best practices. Inhalable dust samples can be analyzed for a variety

of parameters, such as particulate, metals and active pharmaceutical ingredients (APIs). Please note that sampling should be performed by a person who has training in collecting industrial hygiene samples".

IOM Inhalable Dust Sampling NIOSH 0500 - https://www.youtube.com/watch?v=8j8Z1D6goA8. Published on 26 Apr 2017. "The IOM does something that a standard filter cassette does not. It incorporates all particles collected during sampling, even those on the cassette wall. This video reveals the techniques necessary for proper preparation for sampling, placement on the individual and preparation for shipment".

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

17. REFERENCES

AIHA (1998): A strategy for assessing and managing occupational exposures 2nd Edn. AIHA, 1998.

AIHA (2006): A strategy for assessing and managing occupational exposures 3rd Edn. AIHA, 2006.

Aizenberg V, Choe K, Grinshpun SA. (2001). Evaluation of personal aerosol samplers challenged with large particles. Journal of Aerosol Science; 32: 779-793.

BS EN 689:2018 Workplace exposure - Measurement of exposure by inhalation to chemical agents - Strategy for testing compliance with occupational exposure limit values. British Standards Institution.

BS EN ISO 13137:2013 Workplace atmospheres: Pumps for personal sampling of chemical and biological agents. Requirements and test methods British Standards Institution.

BS EN 482:2012+A1:2015: Workplace exposure — General requirements for the performance of procedures for the measurement of chemical agents. British Standards Institution.

BS EN 481:1993 Workplace atmospheres: Size fraction definitions for measurement of airborne particles British Standards Institution.

ECHA (2016) Guidance on Information Requirements and Chemical Safety Assessment, Chapter R.14: Occupational Exposure Assessment, Version 3.0, European Chemicals Agency, Annankatu 18, P.O. Box 400, Helsinki, Finland Fi-00121, August 2016.

ECHA (2015) Guidance on Information Requirements and Chemical Safety Assessment, Chapter R.12: Use description, Version 3.0, European Chemicals Agency, Annankatu 18, P.O. Box 400, Helsinki, Finland Fi-00121, December 2015

ECHA (2012a) Guidance on Information Requirements and Chemical Safety Assessment, Chapter R.14: Occupational Exposure Assessment, Version 2.1, European Chemicals Agency, Annankatu 18, P.O. Box 400, Helsinki, Finland Fi-00121, November 2012.

ECHA (2012b) Guidance on Information Requirements and Chemical Safety Assessment, Chapter R.13: Risk Management Measures and Operational Conditions, Version 1.2, European Chemicals Agency, Annankatu 18, P.O. Box 400, Helsinki, Finland Fi-00121, October 2012.

Galea KS, Searl A, Sánchez-Jiménez A, WoldbæK T, Halgard K, Thorud S, Steinsvåg K, Krüger K, MacCalman L, Cherrie JW, van Tongeren M. (2012) Oil Mist and Vapour Concentrations from Drilling Fluids: Inter- and Intra-laboratory Comparison of Chemical Analyses, Ann. Occup. Hyg; 56(1): 61-69.

HSE (2018) EH40/2005 Workplace exposure limits (Third Edition). HSE Books.

HSE (2014). Methods for Determination of Hazardous Substances (MDHS) 14/4. General methods for sampling and gravimetric analysis of respirable and inhalable dust. URL: http://www.hse.gov.uk/pubns/mdhs/pdfs/mdhs14-4.pdf

IOM, (2011) Development of a standardized method for measuring manganese exposure. IOM Research Report, TM/10/04.

ISO (2012a) ISO 15202-1:2012 Workplace air -- Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry -- Part 1: Sampling.

ISO 15202-2 Workplace air -- Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma atomic emission spectrometry -- Part 2: Sample preparation (Annex G) (ISO, 2012b).

ISO (1995) ISO 7708:1995 Air quality: Particle size fraction definitions for health-related sampling. International Standards Organisation.

ISO 30011:2010 F Workplace air -- Determination of metals and metalloids in airborne particulate matter by inductively coupled plasma mass spectrometry (ISO, 2010).

NTP (2017). NTP Technical Report on the Toxicology and Carcinogenesis Studies of Antimony Trioxide in Wistar HAN Rats and B6C3F1/N Mice. National Toxicology Program, National Institute of Health, U.S Department of Health and Human Services. NTP TR 590.

REACH (2006) Regulation (EC) No 1272/2008 of the European Parliament and of the Council of 18 December 2006 concerning the Registration, Evaluation, Authorisation and Restriction of Chemicals (REACH), establishing a European Chemicals Agency, amending Directive 1999/45/EC and repealing Council Regulation (EEC) No 793/93 and Commission Regulation (EC) No 1488/94 as well as Council Directive 76/769/EEC and Commission Directives 91/155/EEC, 93/67/EEC, 93/105/EC and 2000/21/EC.

Tirez K, Bleux N, Berghmans P (2018). Protocol for the determination of Antimony (Sb) in airborne particulate matter in workplace atmospheres. Study accomplished under the authority of the International Antimony Association 2019/MRG/R/1879.

TRGS 402 (2010) Identification and assessment of the risks from activities involving hazardous substances: Inhalation exposure. GMBl 2010 pp. 231-253 [No. 9]

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

18. ACKNOWLEDGMENTS

This guidance document was drafted for i2a by the IOM, Edinburgh, being informed by similar guidance documents developed for a number of industrial sectors, including Manganese.

Thanks to the i2a Monitoring Task Force for their helpful comments and suggestions during the drafting and finalization of this document. We would also like to thank the participants of the i2a second Technical Workshop held on the 21st February 2019 for their additional comments, which were considered in version 1.2 of this guidance.

APPENDIX 1: SOME EQUIPMENT SUPPLIERS AND INDICATIVE PURCHASE COSTS

To assist companies, some indicative costs are provided with respect to the purchase of routine sampling equipment, as obtained from Casella (info@casellameasurement.com) and SKC (skcinc@skcinc.com). Please note that there other suppliers of sampling equipment, are available. In the event of a companies wishing to purchase any sampling equipment they should contact the supplier directly for a quotation specific to their requirements.

Table 1: Casella equipment purchase costs (prices before VAT and converted into Euros, obtained 3.12.18)

Item	2018 cost (€)
1 x Standard pump Apex 2IS	673.20
1 x One way charger	115.20
1 x 5 way charger	391.20
1 x Kit (case, 5 standard pumps, 5 way charger)	3,747.60
1 x Pro pump Apex2IS	942.00
1 x Kit (case, 5 pro-pumps, 5 way charger)	5,110.80
1 x Calibration adaptor	Cost unavailable
1 x Rotameter	Cost unavailable
1 x Tubing for one pump (1 m)	12.00
1 x Roll tubing 50 feet	73.20
1 x IOM Sampling head & cassette (inhalable)	45.60
1 x Cyclone	46.80
1 x Belt	18.00

Table 2: SKC equipment purchase costs (prices before VAT and converted into Euros, obtained 3.12.18)

Item	2018 cost (€)
1 x Standard pump SideKick	510.0
1 x One way charger	72.00
1 x 5 way charger	288.00
1 x Kit (case, 5 standard pumps, 5 way charger, tubing)	3,222.00
1 x Kit (case, 5 standard pumps, 5 way charger, tubing, 5 IOM sampling heads)	3,582.00
1 x Intermediate pump Sidekick	558.00
1 x Deluxe pump Sidekick	588.00
1 x Calibration adaptor	45.60
1 x Tubing for one pump (1 m)	14.40
1 x Rotameter (0.3-3.4 L min^{-1})	153.60
1 x Roll tubing 15 m	172.80
1 x IOM Sampling head & cassette (inhalable)	45.00
1 x Belt	£20.70

The prices for the standard pump models are given for Casella (Apex 2IS) and SKC (SideKick) and also for the more advanced models (Casella's Apex2IS pro-pump and SKC's intermediate and deluxe pumps) which have extra features e.g. computer interface.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

It is possible to hire sampling equipment from a range of suppliers. IOM is also happy to discuss the hire of equipment required for the measurement campaign and the costs involved. The IOM would require anyone hiring out IOM equipment to complete their 'Agreement for Hire of Equipment' form.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com

About i2a

The mission of the International Antimony Association is to inspire product stewardship along the antimony value chain. This mission is accomplished by generating and sharing information concerning the environmental and health safety and societal benefits of antimony and antimony compounds. Through a common evidence base, i2a promotes a harmonized risk management and continued safe use of antimony and antimony substances across the value chain and geographical borders.

For further information: www.antimony.com.

International Antimony Association (VZW)
Avenue de Broqueville 12, 1150 Brussels, Belgium // +32 (0)2 762 30 93 // info@antimony.com
www.antimony.com