International Platinum Group Metal Association (IPA) Harmonised Methodology for the Sampling of Platinum in Workplace Atmospheres

Background

This method was developed by the IPA Health Science Research Group in collaboration with the University of Wisconsin, Madison, USA by reviewing the available equipment and testing and improving the limits of detection. The method can be used for short-term task (15 minutes) up to 8 hours or more for shift sample collection. It is similar to MDHS 46/2 [1].

1. Equipment

1.1 Sampling equipment

IOM Sampler

The IOM sampler is an inhalable dust sampler suitable for personal sampling - IOM inhalable sampling head (manufactured by SKC U.K. Ltd). The inlet to the device is a 15 mm diameter orifice, pointing outwards from the wearer's chest. The IOM effectively traps particles up to 100 µm in aerodynamic diameter and closely simulates the manner in which airborne workplace particles are inhaled through the nose and mouth.

IOM samplers and cassettes are available in plastic and stainless steel. The stainless steel sampler and cassette is preferred as it reduces the effect of moisture and electro-static electricity.

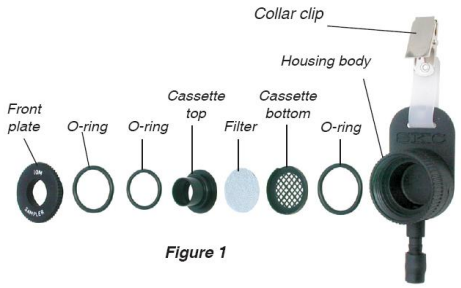


Figure 1

Note: Handling of IOM sampler - Gloves should be worn when handling cassettes and tweezers should be used when working with filters to prevent contamination of the sampling media.

25 mm MCE filters

Filters, of 25 mm diameter, suitable for use in the IOM sampler, with a retentivity of not less than 99.5% for particles with a 0.3 µm diffusion diameter. The use of mixed cellulose ester (MCE) filters of 0.8 µm mean pore diameter are the most suitable. Filters must be "low-metal" grade and batch blank levels should be established on supply. Typical levels observed from "Fisher" catalogue MCE filters gave blanks at < 50 pg Pt from a 10 mL leach test.

If necessary, filters can be pre-cleaned by flow-through leaching using 2x10 mL 0.07 M hydrochloric acid, followed by flow-through rinsing with 3 x 10 mL of high-purity water. It is recommended that this should be carried out in batches and each batch screened to ensure compliance with < 100 pg soluble Pt/filter.

Sampling pumps
Sampling pumps, with an adjustable flow rate, preferably incorporating a flow fault indicator, capable of maintaining the selected flow rate of 2 $Lmin^{-1}$ [2] to within 5% of the nominal value throughout the sampling period and capable of being worn by persons without impending normal work activity. The pumps shall give a pulsation-free flow.

Flowmeter
A portable flowmeter capable of measuring the appropriate flow rate to within ±1 % and calibrated against a primary standard[3].

1.2 Ancillary equipment

- Flexible connection tubing of a diameter suitable for ensuring a leak-proof fit.
- A belt or harness to which the pump can be conveniently fixed, unless the pump is sufficiently small to fit in the worker's pocket.
- Clean flat-tipped forceps (tweezers) for loading and unloading the filters into cassettes.
- IOM transport clip

Figure 2

- IOM calibration adaptor

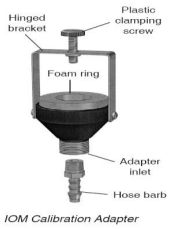


Figure 3

1.3 Analytical equipment

- 0.22 µm MCE syringe filters.
  - Eg. (http://www.elkaylabs.com/13mm-ezee-syringe-filters-022m-pvdf-non-sterile-pr-10.php)
- 10 mL plastic syringes (eg Fisher)
- 15 mL polypropylene centrifuge tubes (eg. Elkay)
- Inductively coupled plasma-mass spectrometry (ICP-MS) (providing the sensitivity necessary to detect low levels of soluble platinum)

1.4 Reagents

- Analytical ultrapure grade hydrochloric acid containing Pt <2 ngL^{-1} eg (Optima grade, Fisher)
- Ultrapure water with a conductivity ~5.5 x 10^{-6} S^{m-1}
- "Citronax" acid detergent or equivalent

2. Procedure

2.1 Sampling

Equipment Cleaning: Disassemble the IOM samplers, soak overnight in 5% solution laboratory detergent, rinse thoroughly with water, wipe with lint free absorptive tissue and allow to dry thoroughly before reassembly. Alternatively, use a laboratory washing machine or ultrasonic bath and perform final rinsing with Ultrapure water

Equipment assembly and calibration: Perform the following in an area where platinum contamination is known to be very low, preferably in a laminar flow fume hood, and wear disposable gloves to prevent the possibility of contamination.

1. Label filter and/or cassette. Load the low-metal MCE filters into clean, dry IOM samplers using clean, flat-tipped tweezers. Assemble sampler. (Appendix 1).
2. Connect each loaded sampler to a sampling pump using clean plastic tubing, ensuring that no leaks can occur.
3. Switch on the pump, attach the calibrated flowmeter to the sampler so that it measures the flow through the sampler inlet orifice, and set the appropriate flow rate with an accuracy of ±5%.
4. Switch off the pump and seal the sampler with its protective cover to prevent contamination with platinum during transport to the sampling position.

Sample Collection: Fix the sampler to the worker, in the breathing zone and as close to the mouth and nose as practicable. Attach the sampling pump to the worker in a manner that causes minimum inconvenience, e.g. to a belt around the waist. When ready to begin sampling, remove the protective cover from the sampler and switch on the pump. Record the time at the start of the sampling period, and if the pump is equipped with an elapsed time indicator, set this to zero.

Note to the worker to please keep the sampler on the outside of clothing or PPE and oriented with the opening straight out from the chest.

Check the pump is functioning and record the flowrate during the sampling if the pump has a rotameter.

For very dusty operations, look at filter during the sampling to check for significant colour change or overloading. If present, a new sample may need to be started for full shift sampling.

Check and record the flowrate during the sampling.

At the end of the sampling period:

1. Measure the flow rate with an accuracy of ±5% using the calibrated flowmeter, switch off the sampling pump, reseal the sampler with its protective cover and record the flow rate and the time.
2. If fitted, observe the reading on the elapsed time indicator. Note - the sample is invalid if the reading on the elapsed time indicator and the timed interval between switching on and switching off the sampling pump do not agree to within ±5%, since this indicates that the pump has not been operating throughout the entire sampling period.
3. In the same low platinum area of the facility used to load the filters, remove the cassette from the sampler, place the cover on the cassette and place into the transport clip provided by the manufacturer.

Record the sample identity and all relevant sampling data on the record sheet (Appendix 2). Calculate the mean flow rate by averaging any flow rate measurements taken throughout the sampling period and calculate the volume of air sampled, in litres, by multiplying the flow rate in litres per minute by the sampling time, in minutes.

With each batch of ten samples, submit for analysis two unused filters from the same pre-cleaned batch/lot of filters used for sample collection. Using the same low platinum area of the facility as used to load the sampling filters, subject these blank filters to exactly the same handling procedure as the samples, but draw no air through them. *The integrity and usefulness of this method, particularly for short duration task-based testing, will be critically dependent on how low these blanks are.*

Transport samples to the approved laboratory in a labelled container suitable to prevent damage or disturbance during transit.

2.2 Laboratory Sample Preparation

Open the filter transport container/cassettes and transfer each filter into an individual, 15 mL centrifuge tube using clean plastic flat-tipped tweezers.

For the analysis of 'total platinum' by extraction with *aqua regia*, the reader is referred to MDHS 46/2 [1].

Wash any particulate material adhering to the internal surfaces of the IOM sampler into the centrifuge tube using 1 mL fractions dispensed from an Eppendorf type pipette to a total 5 mL of 0.07 M hydrochloric acid to be used to leach the sample filters. See Note 4 regarding lower sample volumes.

Add the balance of 5 mL of 0.07 M hydrochloric acid to each tube using the pipette, place in an ultrasonic bath and agitate for 30 minutes, without heating, to dissolve the soluble platinum species. Ensure that the sample filters are fully immersed throughout the leach period. See Note 5.

Transfer the leach solution to the barrel of a syringe connected to a 0.22 µm filter cartridge. Rinse the sample filter and tube with three 1 mL aliquots of 0.07 M hydrochloric acid, transferring each aliquot to the syringe. Insert the plunger and filter the leach solution into a labelled centrifuge tube. Remove the plunger and rinse through the syringe and filter twice with further 1 mL aliquots of 0.07 M HCl to achieve a total of 10 mL of leach solution.

2.3 Sample analysis

Analysis of the prepared solution shall be carried out by a regularly manufacturer serviced Inductively Coupled Plasma Mass spectrometer using platinum isotope peak 195 amu. Calibration will use a certifiable (e.g. NIST) standard within its certified shelf life, diluted from stock concentration immediately prior to use and matched to the same 0.07M hydrochloric acid concentration as the samples and blanks. Internal standardisation is also recommended for ICP-MS. MDHS 46/2 1 provides additional best practice guidance for the solution analysis.

If the laboratory does not have an established QA procedure, then at least one new filter spiked with a suitable known quantity of a platinum standard shall be included with each batch of up to ten sample filters and taken through the full extraction procedure.

2.4 Reporting

Calculate the concentration of platinum in air, ρ(Pt), in micrograms per cubic metre (μg m^{-3}), using the equation:

$$\rho(Pt) = [\rho(Pt)_1.V_1 .DF_1 - \rho(Pt)_0.V_0 .DF_0] /V$$

where

$\rho(Pt)_0$ is the mean concentration, in ng mL^{-1}, of platinum in the blank solutions
$\rho(Pt)_1$ is the concentration, in ng mL^{-1}, of platinum in the sample solution
V is the volume, in litres, of the air sample
V_0 is the volume, in mL, of the blank solutions, ie 10 mL
V_1 is the volume, in mL, of the sample solution, ie 10 mL
DF_0 is the dilution factor for the blank solutions eg 1
DF_1 is the dilution factor for the sample solutions eg 1

Reporting limits: After handling in a clean facility and using pre-cleaned equipment and filters, a 3-sigma quantification limit of 0.08 ng per filter has been demonstrated. This equates to a 3-sigma 0.08 ngM^{-3} quantification limit for an 8 hour sample at 2 $Lmin^{-1}$. (Or 0.17 ng m-3 quantification limit for 4 hours; 2.7 ng m-3 quantification limit for 15 minutes.)."

2.5 Test Report

The test report should include at least the following information:
(a) a complete identification of the air sample, including the date of sampling, the exact place of sampling, the task(s) being undertaken during sampling according to the IPA Task Codes (To be confirmed by Workplace Team) and the identity of the individual whose breathing zone was sampled (Appendix 2);
(b) a reference to this procedure and a description of any deviation from the procedures described;
(c) type and diameter of filter used;
(d) type of sampler used;
(e) type of sampling pump used;
(f) type of flowmeter used, the primary standard against which it was calibrated, and the range of flow rates for which the flowmeter was calibrated;
(g) the %w/w recovery of platinum from any spiked filter;
(h) 'Not detected' results will be reported as the Limit of Detection (LoD); calculated as three times the mean value of the blanks.

IPA-Health Science Research Group
May 2015

Notes and References

1.Methods for the Determination of Hazardous Substances: MDHS 46/2 *Platinum metal and soluble platinum compounds in air*. Health and Safety Executive, Bootle, United Kingdom (December 1996). Available at http://www.hse.gov.uk/pubns/mdhs/pdfs/mdhs46-2.pdf

2. The 2 $Lmin^{-1}$ flowrate is suitable for 8 hour shift sampling. Subject to validation, this may increase in future to allow shorter duration sampling periods which still achieve acceptable accuracy and precision.

3. The flowmeters supplied in pumps are not considered sufficiently accurate for this procedure.

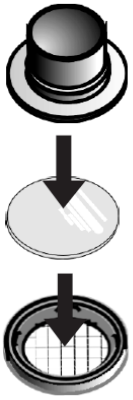
4. When using 0.07 M hydrochloric acid as the extractant, trials using spiking and by analysing field collected samples concluded that 60 minutes gave higher recoveries than 30 minutes extraction times and that sonication gave even higher recoveries; compared to a mechanical shaker. A pragmatic compromise of 30 minutes sonication is recommended.

5. Lower extraction volumes and hence lower detection limits may be possible should they be necessitated by local requirements or future regulations.

APPENDIX 1 – IOM sampler description and user notes

Loading a filter into the IOM cassette

1. Press gently to separate the two halves of the cassette (Figure)
2. Mark the filter with a unique identification number prior to placing the filter in the IOM cassette.
3. Place a 25 mm MCE 0.8 µm filter into the cassette rear (on the support grid). Snap the cassette front into the cassette rear ensuring a tight fit.

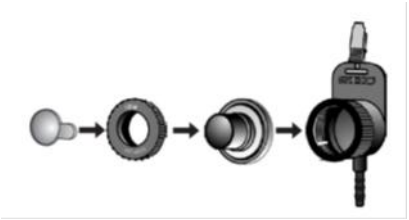


Transporting loaded cassettes

Loaded cassettes can be transported in two ways:

1. Place the IOM cassette into the transport clip as shown in the figure below. Ensure that the cassette cover is in place.

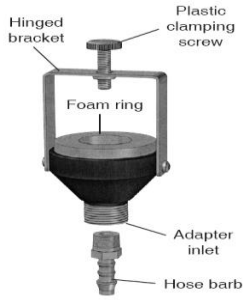
2. An alternative is to insert the cassette into an IOM body and place the cover on the cassette for transport as shown in the figure below.



IOM Setup

Use an IOM calibration adapter to ensure accurate calibration. The setup of the calibration adapter is as follow:

1. Push the IOM through hinged bracket and place the inlet against the foam ring.
2. Clamp the IOM in place with the plastic clamping screw until the foam ring compresses by 1mm. Ensure that the IOM inlet is centred.
3. Screw the supplied hose barb into the threaded hole in the calibration adapter inlet.
4. Use a length of flexible tubing to connect the hose barb to the calibrator outlet.
5. Connect the IOM outlet to the inlet of a sample pump.



IOM Calibration Adapter

Pump flow rate calibration

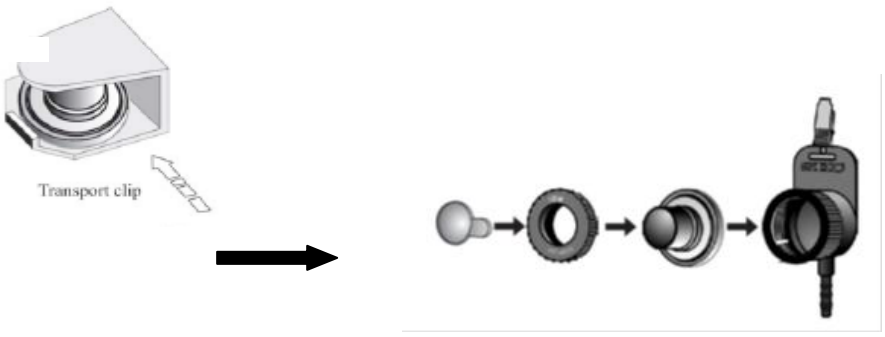
Calibrate the pump flow rate using the IOM calibration adapter accessory and a representative IOM sampler in line. The procedure to follow is described below:

1. Insert the IOM with filter cassette and filter into the calibration adapter (as discussed above)
2. Adjust the pump flow rate to 2l/min
3. Disconnect the representative IOM from the pump and calibrator.

Sampling

Note: Always wear gloves when handling cassettes

1. Remove a newly loaded cassette from its transport clip and remove the cassette cover. Insert the cassette into a clean IOM sampler body. Screw on the front cover as shown in the figure below.



2. Clip onto a worker's clothing in the breathing zone, as shown below.

3. Ensure that the outlet of the IOM sampler is connected to the inlet of a sample pump calibrated to 2 $Lmin^{-1}$.

4. Sample for the time specified by the method.

5. After sampling, remove the cassette from the sampler, place the cover on the cassette and wipe the external surface of the cassette with a clean lint-free paper, cloth, or soft brush. Place the cassette with cover into the transport clip.

APPENDIX 2 – Platinum sampling record sheet

Sample number	Facility or Site:	
	Operation:	
	Workplace / Location:	

Sampled by:		Contact #:		Sampling date:	

Contaminant or analyte:		Shipping date:	
Sampling method:	IPA Workplace Sampling Method		

Personal sample	Yes	No	Area sample:	Yes	No

Employee name:		Description of sample location:
Co #:		
Job title:		
Occupational code:		

PPE:		Ventilation & other controls:
Type	Effectiveness	

Chemicals, materials involved? (Mix name, product name, etc.)
Job description, tasks, work location(s)

Workplace conditions:							
		Indoor		Outdoor		Underground	

WB temp		DB temp		G temp		WBGT	

Humidity:		Airflow:		Weather conditions:	

Sampling data:

Pump number:		Sample media:	
		Sampler:	

Time on:	
Time off:	
Total time:	min

Shift:	

Blank sample reference	

Flow rate:	l/min

Pump checks and adjustments notes:

Volume:	litres

Laboratory to be used:
Interferences and comments to Laboratory:

Pre-sampling calibration record:

Pump Mfg. & number:	

Voltage checked?	Yes	No	Location:	

Flow rate calculation:	
	Flow rate:

Date:	
Time:	

Method:	

Post-sampling calibration record:

Location:	

Flow rate calculation:	
	Flow rate:

Date:	
Time:	