



Challenge

Multi-element analysis of filter dusts is of interest to determine the presence of harmful substances in the workplace. For compliance with lowest emission limit values, while dealing with high matrix and/or acid loads of the digested dust samples, a sensitive and robust analytical technique is required.

Solution

The PlasmaQuant MS Q allows for a robust, sensitive, and accurate multi-element analysis of relevant workplace hazardous substances in digested filter dusts. It offers a routine analysis of filter dusts for risk assessment studies of air quality by emission labs.

Measuring Toxic Elements in Workplace Filter Dusts According to EN 14385 Using ICP-MS

Introduction

The exposure to fine particles by working with dust or dust producing materials can be a health hazard through inhalation. For a reliable exposure-risk assessment at workplaces, it is necessary to monitor emitted dust and its harmful components. This includes the determination of particle sizes of the dust fractions. Dusts are divided into inhalable ($< 100 \mu\text{m}$ aerodynamic diameter) and alveolar ($\leq 10 \mu\text{m}$ aerodynamic diameter) fractions, whose legally defined emission limit values must be observed according to EN 481^[1]. Furthermore, the mass concentration of metals and metalloids in the dusts is a subject of regulation (EN 14385^[2]). For this purpose, dusts are collected by filters, their analytes are transferred into solution via digestion or extraction, and are subsequently quantified in the lab. The collection media are filters (fiberglass, fiber quartz glass, teflon, membrane) and foams. The quality and purity of the collection media are crucial to the quality of the analysis. Depending on the filter constitution, homogeneity, and

resistance to acids and other solvents, high filter blanks of certain elements may occur during the analysis. In addition, the purity of the chemicals used is decisive for reaching the lowest detection limits. The preparation process depends on several factors (e.g., filter material, collected dust quantity, particle size, digestion procedure).^[3, 4]

Due to occasionally high acid and/or matrix loads next to lowest stipulated detection limits, a robust and sensitive analysis system is required. ICP-MS fulfills these requirements, allowing fast, robust, and sensitive multi-element analysis. Certified reference materials (CRMs) can be used for internal quality control of the analysis method. With this application note, we demonstrate the robust and sensitive determination of metal and metalloid profiles in four certified reference materials with the PlasmaQuant MS Q, showing its exemplary capability for routine analysis of filter dusts in emission testing labs.

Materials and Methods

Samples and reagents

Table 1: Sample material

Sample label	Sample type	Weighed portion [mg]	
		A	B
CRM BCR® - 038	Fly ash from pulverized coal*	8.49	7.78
CRM BCR® - 176R	Fly ash**	9.96	8.87
CRM HLNUG 43601	Blast furnace slag***	9.31	8.62
CRM HLNUG 43606	Blast furnace slag***	13.43	11.86

* prepared from fly ash collected at the electrostatic precipitator of a pulverized coal-fired power station

** prepared from a fly ash collected in the electrostatic filters of a city waste incineration plant

***blast furnace slag of an emission simulation apparatus (ESA) spiked with heavy metals; main constituents: SiO₂, Al₂O₃, Fe₂O₃, CaO, amorphous iron and aluminosilicates

The CRMs (Table 1) were microwave digested using 8 mL nitric acid (HNO₃, supra-pure) and 2 mL hydrofluoric acid (HF, supra-pure). Subsequently, 20 mL saturated boric acid (H₃BO₃, pure) and 15 mL ultra-pure water were added for complexation of the remaining HF and topped up to a final volume of 50 mL. Two independent digestions were done for each certified reference material (duplicates A and B). The weighed portions are listed in Table 1. This digestion procedure is compliant with EN 22022-1^[5]. A suitable digestion procedure for the speedwave XPERT microwave is provided by Berghof Products + Instruments^[6].

The samples were prepared and diluted 1000-, 100-, 10-, and 5-fold. In order to correct long-term signal drifts and matrix effects, 10 µg/L of Y, Rh, Tb, and Ir were added as internal standards online via a Y-piece. For sample introduction via the peristaltic pump black/black PVC tubings (0.030 mm ID) for samples and orange/green PVC tubings (0.015 mm ID) for the internal standard solution were used. For calibration, blanks, rinsing, and sample dilution, a mixture of 1% nitric acid (HNO₃, ultra-pure, distilled) and 0.1% hydrochloric acid (HCl, ultra-pure) was used to ensure

analyte stability. To stabilize Hg and avoid memory effects, 100 µg/L Au (Merck, 1 g/L) was added to all solutions.

Calibration

Calibration solutions were prepared in a 1% HNO₃ / 0.1% HCl solution using a multi-element standard (TraceCERT® Periodic Table Mix 1 for ICP, 10 mg/L) and single element standards (Hg: CPAchem, 1000 mg/L; Sb: TraceCERT®, 1000 mg/L). Calibration concentrations were 0.1 – 0.5 – 1.0 – 10.0 – 100.0 µg/L. Hg was calibrated with 0.1 – 0.5 – 1.0 – 3.0 µg/L.

Instrumentation

A PlasmaQuant MS Q was equipped with an autosampler (ASX-560, CETAC) with enclosure and HEPA filter, 4-channel peristaltic pump, MicroMist™ (0.4 mL/min) nebulizer, Scott double-pass spray chamber, 2.4 mm injector torch, platinum tipped sampler, and skimmer cones. Sample preparation and measurements were carried out in a routine analytical laboratory, and not under clean room conditions.

Table 2: Instrument configuration – PlasmaQuant MS Q

Parameter	Specification
Nebulizer	MicroMist™ (0.4 mL/min)
Spray chamber	Peltier cooled quartz glass Scott double-pass
Torch	Fassel torch with 2.4 mm injector
Cones	Pt tipped sampler and skimmer cone
iCRC gases, flow	H ₂ – 80 mL/min; He – 120 mL/min
Auto sampler	ASX-560 (CETAC), enclosure with HEPA filter

Method parameters

Table 3: Method parameters

Parameter	Specification
Plasma gas flow	9.0 L/min
Auxiliary gas flow	1.2 L/min
Sheath gas flow	0.0 L/min
Nebulizer gas flow	1.00 L/min
RF power	1.35 kW
Sampling depth	5.0 mm
Pump rate	13 rpm
Stabilization delay (condition set)	20 s (H2), 12 s (nG), 15 s (He) *
Spray chamber temperature	3 °C

* Please consider that short switching times between the measuring modes of < 5 s can be chosen. Here, to the benefit of the best possible measuring precision, higher stabilization times were selected, achieving RSDs of in average < 2%.

Evaluation parameters

For data recording, five average values (replicates) were calculated, each average composed of twenty single scans. The resulting mean value and standard deviation were obtained from the average of the five replicates. Pb was determined using the sum of the intensities for its three major isotopes (^{206}Pb , ^{207}Pb , ^{208}Pb) to account for isotopic variation in the samples and standards. For internal standard correction ^{89}Y , ^{103}Rh , ^{159}Tb , and ^{193}Ir were chosen.

For the removal of polyatomic interferences with certain analytes, Analytik Jena's iCRC technology was used, applying helium collision gas and hydrogen reaction gas. In addition, no-gas-mode was applied for isotopes that have no interference with polyatomic ions. Therefore, three different analysis conditions were applied within one measurement: no-gas-mode, hydrogen mode, and helium mode. The expected polyatomic interferences for selected isotopes and the chosen iCRC gasses for interference removal are listed in Table 4.

Table 4: Selected isotopes, their expected polyatomic interferences, and chosen iCRC gas for interference removal

Isotope	Expected interference	iCRC gas
⁵¹ V	³⁵ Cl ¹⁶ O ⁺	He
⁵² Cr	³⁶ S ¹⁶ O ⁺ , ³⁶ Ar ¹⁶ O ⁺ , ⁴⁰ Ar ¹² C ⁺	He
⁵⁵ Mn	³⁹ K ¹⁶ O ⁺ , ¹⁵ N ⁴⁰ Ar ⁺	He
⁵⁹ Co	⁴³ Ca ¹⁶ O ⁺ , ²⁴ Mg ³⁵ Cl ⁺	He
⁶⁰ Ni	⁴⁴ Ca ¹⁶ O ⁺	He
⁶³ Cu	⁴⁰ Ar ²³ Na ⁺ , ⁴⁷ Ti ¹⁶ O ⁺ , ²³ Na ⁴⁰ Ca ⁺ , ⁴⁴ Ca ¹⁹ F ⁺	He
⁶⁶ Zn	⁵⁰ Ti ¹⁶ O ⁺ , ⁵¹ V ¹⁶ O ⁺ , ²⁶ Mg ⁴⁰ Ar ⁺ , ³¹ P ³⁵ Cl ⁺ , ³² S ³⁴ S ⁺	He
⁷⁵ As	⁴⁰ Ar ³⁵ Cl ⁺	H ₂
⁷⁸ Se	³⁸ Ar ⁴⁰ Ar ⁺ , ³⁸ Ar ⁴⁰ Ca ⁺	H ₂
¹¹² Cd	-	None
¹²¹ Sb	-	None
²⁰² Hg	-	None
²⁰⁵ Tl	-	None
²⁰⁶⁻²⁰⁸ Pb	-	None

Results and Discussion

Element concentrations

Table 5 shows the measured element concentrations resulting from independent duplicates and several dilutions, as well as the reference concentrations of the certified materials.

Table 5: Measured element concentrations (rounded to three significant digits) with certified concentrations in parentheses

Isotope [Mode]	BCR-038 [mg/kg]	BCR-176R [mg/kg]	HLNUG 43601 [mg/kg]	HLNUG 43604 [mg/kg]
⁷⁵ As [H ₂]	48.1 (48 ± 2.3)	55.4 (54 ± 5)	32.6 (n. s.)	28 (n. s.)
⁷⁸ Se [H ₂]	18.2 (n. s.)	18 (18.3 ± 1.9)	6.53 (n. s.)	6.52 (n. s.)
¹¹² Cd [nG]	4.39 (4.6 ± 0.3)	213 (226 ± 19)	2370 (2390 ± 53)	1700 (1703 ± 41)
¹²¹ Sb [nG]	9.34 (n. s.)	876 (850 ± 50)	12 (n. s.)	11.4 (n. s.)
²⁰² Hg [nG]	2.15 (2.1 ± 0.15)	1.6 (1.6 ± 0.23)	<IDL (n. s.)	<IDL (n. s.)
²⁰⁵ Tl [nG]	2.55 (n. s.)	1.45 (1.32 ± 0.21)	1.7 (n. s.)	1.5 (n. s.)
²⁰⁶⁻²⁰⁸ Pb [nG]	267 (262 ± 11)	5070 (5000 ± 500)	4490 (4498 ± 125)	8950 (8972 ± 196)
⁵¹ V [He]	343 (334 ± n. s.)	35.7 (35 ± 6)	1860 (1929 ± 94)	1290 (1273 ± 27)
⁵² Cr [He]	188 (192 ± 10)	866 (810 ± 70)	5020 (5035 ± 162)	5750 (5694 ± 109)
⁵⁵ Mn [He]	466 (479 ± 16)	708 (730 ± 50)	4200 (4217 ± 139)	3860 (3922 ± 80)
⁵⁹ Co [He]	53.5 (53.8 ± 1.9)	26.5 (26.7 ± 1.6)	2260 (2275 ± 66)	5770 (5727 ± 127)
⁶⁰ Ni [He]	199 (194 ± n. s.)	116 (117 ± 6)	3470 (3508 ± 85)	4710 (4684 ± 96)
⁶³ Cu [He]	173 (176 ± 9)	1070 (1050 ± 70)	4880 (4870 ± 138)	6120 (6195 ± 131)
⁶⁶ Zn [He]	571 (581 ± 29)	16900 (16800 ± 400)	269 (n.s.)	214 (n.s.)

H₂ – hydrogen mode

nG – no gas mode

He – helium mode

n. s. – not specified

Detection and quantification limits

Table 6 shows instrument detection and quantification limits (IDL, IQL), determined on the basis of the standard deviation of the blank and the slope of the calibration curve according to EN 32645^[7]. The method detection limits (MDL) were

calculated with respect to the weighed portions of the solids and filling volume. Due to the diversity and variety of concentrations from the several dilution steps, the dilution factors are not considered here.

Table 6: Detection and quantification limits (rounded to three significant digits)

Isotope [Mode]	IDL [µg/L]	IQL [µg/L]	MDL							
			BCR-038 [µg/kg]		BCR-176R [µg/kg]		HLNUG 43601 [µg/kg]		HLNUG 43604 [µg/kg]	
			A	B	A	B	A	B	A	B
⁷⁵ As [H ₂]	0.0217	0.0725	0.128	0.139	0.109	0.122	0.117	0.126	0.0808	0.0915
⁷⁸ Se [H ₂]	0.0467	0.156	0.275	0.3	0.234	0.263	0.251	0.271	0.174	0.197
¹¹² Cd [nG]	0.0015	0.0051	0.00824	0.009	0.00703	0.00789	0.00752	0.00812	0.00521	0.0059
¹²¹ Sb [nG]	0.0025	0.0082	0.0147	0.0161	0.0126	0.0141	0.0134	0.0145	0.00931	0.0105
²⁰² Hg [nG]	0.0039	0.013	0.023	0.0251	0.0196	0.022	0.0209	0.0226	0.0145	0.0164
²⁰⁵ Tl [nG]	0.0002	0.0008	0.00118	0.00129	0.001	0.00113	0.00107	0.00116	0.000745	0.000843
²⁰⁶⁻²⁰⁸ Pb [nG]	0.0024	0.008	0.0141	0.0154	0.012	0.0135	0.0129	0.0139	0.00894	0.0101
⁵¹ V [He]	0.0291	0.0971	0.171	0.187	0.146	0.164	0.156	0.169	0.108	0.123
⁵² Cr [He]	0.0240	0.0802	0.141	0.154	0.12	0.135	0.129	0.139	0.0894	0.101
⁵⁵ Mn [He]	0.0099	0.0331	0.0583	0.0636	0.0497	0.0558	0.0532	0.0574	0.0369	0.0417
⁵⁹ Co [He]	0.0016	0.0054	0.00942	0.0103	0.00803	0.00902	0.00859	0.00928	0.00596	0.00675
⁶⁰ Ni [He]	0.0157	0.0522	0.0925	0.101	0.0788	0.0885	0.0843	0.0911	0.0585	0.0662
⁶³ Cu [He]	0.0222	0.0741	0.131	0.143	0.111	0.125	0.119	0.129	0.0827	0.0936
⁶⁶ Zn [He]	0.0240	0.0802	0.148	0.161	0.126	0.141	0.135	0.146	0.0934	0.106

H₂ – hydrogen mode

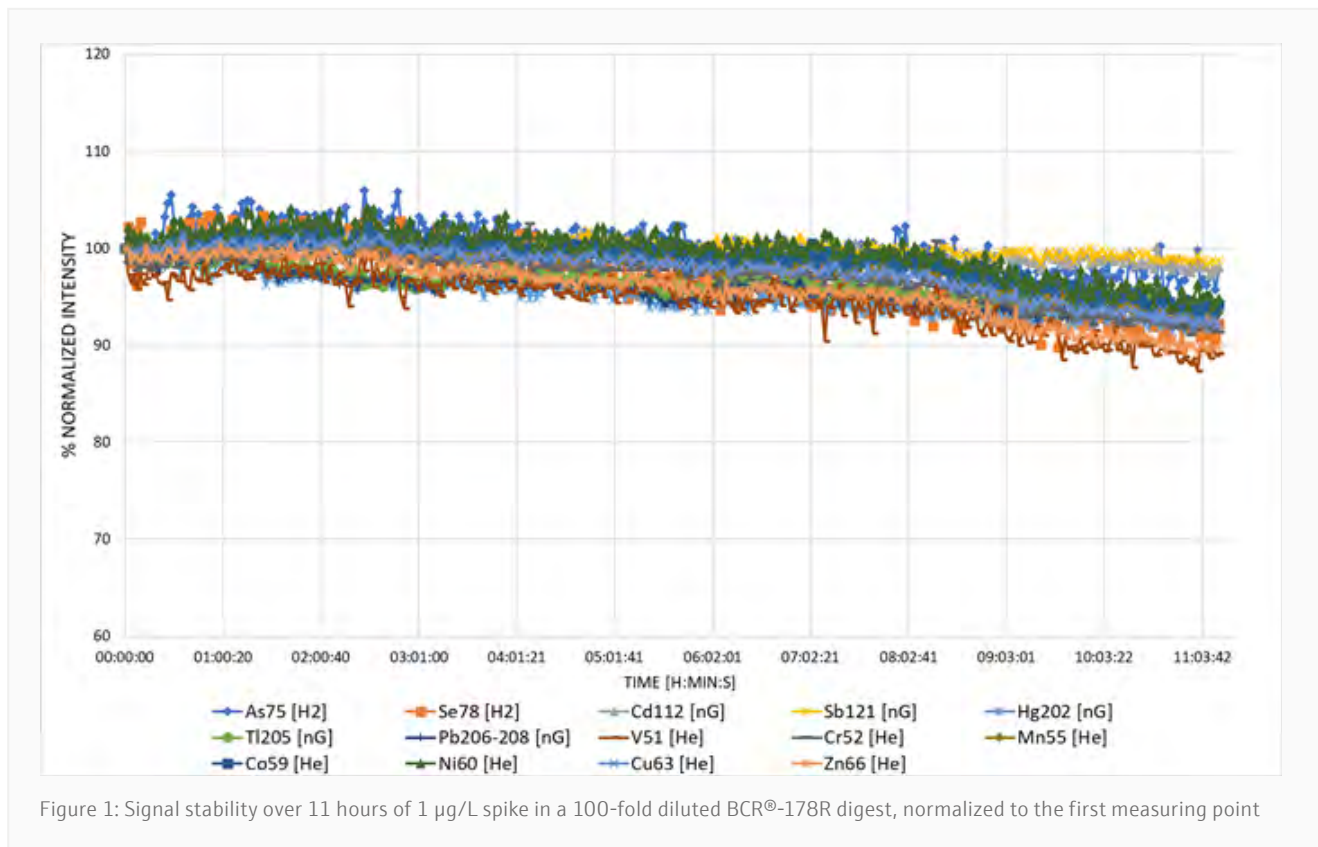
nG – no gas mode

He – helium mode

Long-term stability

The BCR®-176R digest (A) was diluted 100-fold, spiked with 1 µg/L of each element of interest and repeatedly measured via self-aspiration (no internal standard addition and correction) over 11 hours, generating 358 data points. The signal stability, normalized to the first measuring point,

is shown in Figure 1. The overall signal deviation of 10% and the relative standard deviation of the respective signals of 0.75 to 4.4% indicate the good instrument precision and robustness.



Conclusion

The PlasmaQuant MS Q offers a precise, sensitive, and cost-efficient routine trace analysis of filter dust. It offers suitable analytical capabilities for routine risk assessment studies of air quality by emission labs according to EN 14385. The PlasmaQuant MS Q includes several innovative technologies (Eco Plasma, ReflexION ion mirror, iCRC, pre-quadrupole fringe rods, all-digital detector) that provide the following advantages:

- The high sensitivity enables the achievement of lowest detection limits over the entire mass range allowing compliance with lowest emission limit values. The benefit of this high sensitivity is that matrix-matched calibration, in terms of matrix effects, can simply be replaced by sample dilution. This enables high flexibility in measuring different matrices within the same sequence.
- If correctly stabilized, Hg can be measured together with all other elements of interest within the same run due to the outstanding sensitivity. This avoids the need for additional Hg measurements on other instruments (e.g., AAS).
- The excellent plasma robustness allows long-term measurement stability while low Ar consumption of 11 L/min total is implemented for low running costs.
- The iCRC (integrated Collision Reaction Cell) combines collision and reaction mode within one run to remove polyatomic interferences for accurate quantification. Fast

switching times between the modes allow rapid sample analysis.



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