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► To cite this version:

Marsailidh Twigg, Chiara Di Marco, Elizabeth Mcghee, Christine Braban, Eiko Nemitz, et al.. The potential of high temporal resolution automatic measurements of PM_{2.5} composition as an alternative to the filter-based manual method used in routine monitoring. *Atmospheric Environment*, 2023, 315, pp.120148. 10.1016/j.atmosenv.2023.120148 . hal-04252689

HAL Id: hal-04252689

<https://hal.science/hal-04252689>

Submitted on 5 Mar 2024

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The potential of high temporal resolution automatic measurements of PM_{2.5} composition as an alternative to the filter-based manual method used in routine monitoring

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Abstract

Under the EU Air Quality Directive (AQD) 2008/50/EC member states are required to undertake routine monitoring of PM_{2.5} composition at background stations. The AQD states for PM_{2.5} speciation this should include at least: nitrate (NO₃⁻), sulfate (SO₄²⁻), chloride (Cl⁻), ammonium (NH₄⁺), sodium (Na⁺), potassium (K⁺), magnesium (Mg²⁺), calcium (Ca²⁺), elemental carbon (EC) and organic carbon (OC). Until 2017, it was the responsibility of each country to determine the methodology used to report the composition for the inorganic components of PM_{2.5}. In August 2017 a European standard method of measurement of PM_{2.5} inorganic chemical components (NO₃⁻, SO₄²⁻, Cl⁻, NH₄⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺) as deposited on filters (EN16913:2017) was published. From August 2019 this then became the European

44 standard method. This filter method is labour-intensive and provides limited time resolution
45 and is prone to losses of volatile compounds. There is therefore increasing interest in the use of
46 alternative automated methods. For example, the UK reports hourly PM_{2.5} chemical
47 composition using the Monitor for AeRosols and Gases in Ambient air (MARGA, Metrohm,
48 NL). This study is a pre-assessment review of available data to demonstrate if or to what extent
49 equivalence is possible using either the MARGA or other available automatic methods,
50 including the Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research Inc. US) and
51 the Ambient Ion Monitor (AIM, URG, US).

52 To demonstrate equivalence three objectives were to be met. The first two objectives focused
53 on data capture and were met by all three instruments. The third objective was to have less than
54 a 50% expanded uncertainty compared to the reference method for each species. Analysis of
55 this objective was carried out using existing paired datasets available from different regions
56 around the world. It was found that the MARGA (2006 to 2019 model) had the potential to
57 demonstrate equivalence for all species in the standard, though it was only through a
58 combination of case studies that it passed uncertainty criteria. The ACSM has the potential to
59 demonstrate equivalence for NH₄⁺, SO₄²⁻, and in some conditions NO₃⁻, but did not for Cl⁻ due
60 to its inability to quantify refractory aerosol such as sea salt. The AIM has the potential for
61 NH₄⁺, NO₃⁻, SO₄²⁻, Cl⁻ and Mg²⁺. Future investigations are required to determine if the AIM
62 could be optimised to meet the expanded uncertainty criterion for Na⁺, K⁺ and Ca²⁺.

63 The recommendation is that a second stage to demonstrate equivalence is required which would
64 include both laboratory and field studies of the three candidate methods and any other
65 technologies identified with the potential to report the required species.

66 Keywords: PM_{2.5}, inorganic aerosol, ACSM, HR-TOF-AMS, MARGA, AIM

67 1. Introduction

68 Particulate matter of 2.5 μm (PM_{2.5}) in aerodynamic diameter or less is of concern to human health. Epidemiological studies
69 have so far been unable to demonstrate if it is chronic exposure to total PM or individual compounds contained within PM_{2.5},
70 which are detrimental to health, and to establish different toxicities for different aerosols. As such the World Health
71 Organisation (WHO) concluded in the Review of Health Aspects of Air Pollution (REVIHAAP) ¹ that any long term exposure
72 to PM_{2.5} is a threat to human health and encourages nations to reduce PM exposure.

73 In Europe, the revised EU Air Quality Directive (AQD) 2008/50/EC² on ambient air quality and cleaner air in Europe
74 specifies that member states are required to carry out measurements of PM_{2.5} total mass and concentrations of appropriate
75 compounds to characterise its chemical composition. The AQD states for PM_{2.5} speciation this should include at least: nitrate
76 (NO₃⁻), sulfate (SO₄²⁻), chloride (Cl⁻), ammonium (NH₄⁺), sodium (Na⁺), potassium (K⁺), magnesium (Mg²⁺), calcium (Ca²⁺),
77 elemental carbon (EC) and organic carbon (OC). The AQD requires measurements to be carried out at rural background sites
78 to better understand the impacts and sources of pollutants in order to develop appropriate policies. Member states are also
79 required, where possible, to co-ordinate measurements with those of the cooperative programme for monitoring and evaluation
80 of the long-range transmission of air pollutants in Europe (EMEP) which was set-up under the 1979 UNECE Convention on
81 Long-range Transboundary Air Pollution (CLRTAP) ³. At the time when this requirement was introduced into the revised AQD,
82 there was no standard method defined to characterise the chemical composition of PM_{2.5} and as a result each country determined
83 how this requirement of the AQD would be addressed.

84 The UK had already established two EMEP Supersites (Level II/III) prior to the AQD being transposed into UK law. For
85 Level II sites, the EMEP Monitoring Strategy requests artefact-free methods to distinguish between the gas and aerosol phase
86 of ammonia (NH₃/NH₄⁺) and nitric acid (HNO₃/NO₃⁻) compounds. This is not possible with the simple filter sampler of the
87 reference method (RM) and is typically achieved through 24-hour samplers consisting of denuder-filter-pack sampling trains⁴.
88 These are labour intensive to operate and the daily time-resolution does not provide any information on diel cycles. Instead, the
89 UK chose to adopt the Monitor for AeRosols and Gases in Ambient air (MARGA, Metrohm, NL) system. The dual channel
90 MARGA system deployed in the UK simultaneously provides hourly data on water-soluble inorganic speciated PM₁₀ and PM_{2.5}
91 (NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻ and SO₄²⁻), as well as the gases ammonia (NH₃), nitric acid (HNO₃), nitrous acid (HONO),
92 sulphur dioxide (SO₂) and hydrochloric acid (HCl) in one single instrument⁵.

93 In August 2017, however, a standard method of measurement of NO₃⁻, SO₄²⁻, Cl⁻, NH₄⁺, Na⁺, K⁺, Mg²⁺, Ca²⁺ in PM_{2.5} as
94 deposited on filters (EN16913:2017) was published⁶. From August 2019 this then became the reference method. The new

95 standard requires sampling for 24 hours onto filters using the sampling protocol that is laid out in the EN12341:2014 standard
96 for measuring total PM₁₀ and PM_{2.5} mass. The EN16913:2017 standard describes how these samples are to be stored and
97 analysed off line by ion chromatography in order to determine PM_{2.5} speciation of inorganic ions. The cations (excluding NH₄⁺)
98 can also alternatively be analysed by inductively coupled plasma optical emission spectrometry (ICP-OES) and the NH₄⁺
99 analysed alternatively by photometry or conductometry. The EN16913:2017 standard acknowledges that the method can be
100 subject to losses due to sample evaporation of volatile species. It states that for NO₃⁻, NH₄⁺ and Cl⁻, there could be an
101 underestimation of up to 30% due to evaporational losses of ammonium nitrate and chloride (NH₄NO₃, NH₄Cl) during filter
102 sampling.

103 There are however alternative automatic methods (sampling and analysis online), which report all or some of the PM_{2.5}
104 species required by both the AQD and EMEP. These methods include the MARGA, (Metrohm, NL)^{5,7-9}, the Aerosol Ion
105 monitor (AIM, URG, ThermoFisher, US)^{10,11} and the Aerosol Chemical Speciation Monitor (ACSM, Aerodyne Research Inc.,
106 US)^{12,13,13-15}, which are increasingly being used for routine monitoring around the world.

107 Ideally all equipment used in reporting should follow the the RM or is able to demonstrate equivalence using an alternative
108 method as described under the Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods¹⁶. To carry out
109 an equivalence study there are four phases (refer to Table S1 for further details), the first phase being a non experimental pre-
110 assessment to check whether the candidate methods (CM) have the potential for fulfilling the data quality objectives in the
111 directive on the data capture, as well as the measurement uncertainty, which is set by this study¹⁶. This study represents this
112 first phase to provide evidence that the automatic methods (MARGA, AIM, ACSM/HR-TOF-AMS) used in routine monitoring
113 should be considered for future equivalence studies for the EN16913:2017 standard. It is however noted that EN16913:2017 is
114 only recently published and there is currently no requirement yet to implement the standard under the AQD.

115 2. Methods

116 2.1 Description of candidate methods (CMs)

117 In this study a total of three methods are proposed as CMs for the EN12341:2014. The first two (MARGA and AIM) utilise
118 the same analytical (ion chromatography) principle used in the RM, but are coupled to a system for real-time automated sample
119 collection and analysis. Both wet chemistry systems scrub the gas phase from the sample first and there is no possibility of
120 aerosol volatilisation once in the liquid phase, thus minimising positive and negative sampling artefacts, respectively.

121 The MARGA (Metrohm, NL) measures simultaneously water soluble aerosols (NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, NO₃⁻ and
122 SO₄²⁻) and trace gases (NH₃, HNO₃, HONO, SO₂ and HCl) at hourly resolution. The instrument first captures gases in a wet
123 rotating denuder¹⁷ (WRD) and then water soluble aerosols with a steam jet aerosol collector¹⁸ (SJAC) reporting concentrations
124 with hourly resolution. Currently there are two versions of the MARGA, the original MARGA (available commercially 2006
125 to 2019) and the 2060 MARGA (available commercially from 2019). For the purpose of this study only the original MARGA
126 design is assessed, as no data was available on the performance of the MARGA 2060. In the typical configuration, the system
127 measures the following constituents of particulate matter outlined in the EN16913:2017 standard: NH₄⁺, Na⁺, K⁺, Ca²⁺, Mg²⁺,
128 Cl⁻, NO₃⁻ and SO₄²⁻. The PM size cut off is determined by the inlet type and flow rate chosen by the operators and therefore
129 varies between case studies. Table 1 reports the set-ups used in each case. A full description of the method and quality
130 assurance/quality control (QA/QC) protocol used in the UK can be found in Twigg *et al.* (2015)⁵ and detection limits are listed
131 in Supplementary Information, Table S2.

132 The Ambient Ion Monitor (AIM) 9000-B used in this study provides hourly resolution of particulate anion (Cl⁻, NO₃⁻ and
133 SO₄²⁻) and cation (Na⁺, NH₄⁺, K⁺, Mg²⁺ and Ca²⁺) concentrations¹¹. To sample, the ambient air is drawn through a membrane-
134 style Liquid Diffusion Denuder where interfering acidic and basic gases are removed. Aerosol collection is similar to that in
135 the MARGA: in order to achieve high collection efficiencies, the particle-laden air stream next enters the Aerosol Super
136 Saturation Chamber to enhance particle growth. An Inertial Particle Separator collects these enlarged particles, which it then
137 stores in an Aerosol Sample Collector until the particles can be injected into the two ion chromatography systems. A full
138 description of the method and quality assurance (QA) that was used in the UK can be found in Beccaceci *et al.* (2015)¹⁰, with
139 detection limits in the Supplementary Information (Table S3). An alternative model of the AIM (9000-C; not used here)
140 additionally offers analysis of the gases collected by the denuder.

141 The third method utilises mass spectrometry for analysis, which does not rely on water solubility of the target compounds.
142 Instead, it provides real-time measurements of the chemical composition of submicron non-refractory species that volatilise at
143 a temperature of ~600°C^{19,20}. The emerging gases are subsequently ionised by 70 eV electron impact ionisation and detected
144 using a quadrupole or time-of-flight mass spectrometer. Both the High-Resolution Time-of-Flight Aerosol Mass Spectrometer
145 (HR-TOF-AMS) and the Aerosol Chemical Speciation Monitor (ACSM) (both Aerodyne Research Inc., US) operate on this

146 principle. The ACSM is a modification of the AMS which is smaller, at lower cost, easier to analyse and ideal for monitoring
147 purposes, whilst the HR-TOF-AMS additionally provides size information. Further details of the HR-TOF-AMS and ACSM
148 can be found in DeCarlo *et al.* (2006)²⁰ and Ng *et al.* (2011)²¹ respectively and the detection limits in Table S4. HR-TOF-
149 AMS and ACSM have traditionally been operated with the so-called standard lens (transfer inlet into the vacuum system)
150 which approximates PM₁; no paired data were available for instruments using the newer PM_{2.5} lens²².

151 2.2 Test datasets

152 All three automatic methods of interest are or have been used in the UK's air quality monitoring networks. To determine if
153 the first two data quality objectives are met, data was obtained from the UK-Air website for the MARGA (PM_{2.5} from the
154 Auchencorth Moss⁵ and Chilbolton²³ field sites) and AIM (PM₁₀, North Kensington¹⁰) for three calendar years (2016 to 2018).
155 ACSM data from North Kensington^{13,15} using a PM₁ lens for 2 years (2016 to 2017) was obtained directly from Imperial
156 College London (*David Green, personal communication*).

157 To determine if equivalence was possible, paired datasets were obtained from other studies, which had used the proposed
158 CMs compared to filter samples. In total eight case studies were obtained: 1. Revin, France, 2. Barcelona, Spain, 3. Mace
159 Head, Ireland, 4. Melpitz, Germany, 5. Kumpula, Finland, 6. Research Triangle Park, US, 7. San Pietro Capofiume, Italy and
160 8. North Kensington, UK. Details of the set-up and sampling period of each paired dataset are summarised in Table 1,
161 including references to each dataset.

162 2.3 Calculation of equivalence

163 Equivalence is defined under the Terms of Reference for the CEN/TC 264 Ambient Air standards¹⁶. It states that methods
164 other than the RM may be used for implementation of the Directive provided they fulfil the minimum data quality objectives
165 specified in the Directive. Therefore, in this study the priority is to determine if the two air quality objectives of the Directive
166 (2008/50/EC) are met by the CMs. The objectives in Appendix IV of the directive for speciated PM_{2.5} are:

- 167 1. Minimum data coverage = 14% (which equates to 8 weeks over 1 calendar year)
- 168 2. Minimum data coverage over a 24 hour period = 90% (>21.6 hours)

169 In addition, a third data quality objective was set in this study for equivalence to the RM, not currently in the AQD of:

- 170 3. Expanded uncertainty has to be less than 50 %.

171 Here, the expanded uncertainty (W_{cm}) was studied with the methodology set out by CEN/TC 264/WG15, using the tool
172 currently adopted to demonstrate equivalence for total PM monitors²⁴, but is generic enough to be transferrable to other similar
173 PM-based assessments. This compares RMs and CMs in an orthogonal regression analysis to calculate the W_{cm} . If either the
174 slope is found to be significantly different from one and/or the intercept is significantly different from zero in the orthogonal
175 regression, the CM can be calibrated (corrected) using the values obtained in the regression. An orthogonal regression with the
176 corrected CM is then undertaken to determine the W_{cm} . Further details of the methodology can be found in the Guidance for
177 the Demonstration of Equivalence of Ambient Air Monitoring Methods¹⁶ and the tool can be downloaded at
178 <https://ec.europa.eu/environment/air/quality/assessment.htm>. (Refer to Supplementary Material for further details on the
179 calculation of W_{cm}).

180 The following criteria for the W_{cm} analysis have to be met:

181 Criterion 1: The slope (uncorrected or corrected) is not significantly different from one.

182 Criterion 2: The intercept (uncorrected or corrected) is not significantly different from zero.

183 Criterion 3: The expanded uncertainty is less than 50%.

184

185 **Table 1** Description of method set up of paired data sets used to investigate the potential equivalence for the candidate methods for EN16913:2017 standard.*It has
 186 been estimated that due to the inlet set-up that the PM cut-off was approximately 26 μm in aerodynamic diameter. # For specific N for each ion, refer to Figures S1
 187 to S45.

Case study	1	2	3	4	5	6	7	8
Geographical area	Revin, France	Barcelona, Spain	Mace Head, Ireland ²⁵	Melpitz, Germany	Kumpula, Helsinki, Finland	Research Triangle Park, North Carolina, USA	San Pietro Capofiume, Italy	North Kensington, London, UK
Longitude	49° 54' 60" N, 04° 38' 29" E	41° 23' 14.3" N 02° 06' 56.6" E	53° 19' 34" N, 9° 54' 14" W	51°32'N 12°56'E	60°12'11.1"N 24°57'40.7"E	35.89 N 78.87 W	44° 39' N 11° 37' E	51.521050 N -0.213492
Classification	Rural background	Urban background	Rural background	Rural Background	Urban Background	Urban Background	Rural Background	Urban background
Metres above mean sea level (m)	395	80	5	86	26	92	11	5
CM inlet length (m)	2.5	2-3	10 m	3.6	1.7	4	Not available	1 – 2
Inlet material for CM	Stainless steel		Stainless steel sampling duct	Teflon-coated PM10 cyclone and 3.5 m long polyethylene tube	Teflon coated cut-off inlet with polyethylene tubing	Acrylic inertial separator with polyethylene tubing	Teflon coated cyclone with polyethylene tubing	PM ₁₀ head attached to an anodized aluminium tube
Network affiliations	EMEP, ACTRIS, GAW	ACTRIS	EMEP, ACTRIS, GAW	EMEP GAW ACTRIS	Intensive field study	Intensive field study	Intensive field study	UK PNC
Average temperature	4.3°C	18.5°C	-	10.0°C	6.7°C	16.2°C	23.6°C	-
Sampling periods (Maximum number of data points used [#])	30/11/2017 - 30/03/2018 (N = 18)	05/05/2014 - 24/05/2015 and 02/09/2017 - 27/10/2018 (N = 152)	01/01/2009 – 30/12/2012 (N= 385)	01/01/2010 – 31/12/2014 (N=1488)	05/02/2010 – 05/05/2010 (N=86)	08/09/2010 – 08/10/2010 (N=60)	14/06/2012 – 09/07/2012 (N=29)	03/01/2013 – 27/12/2013 (N=33)
Reference Method (RM)	PM _{2.5} 150 mm diameter quartz filters, pre-fired at 500 degC during 24 hours. Digitel DA80 equipped with a Digitel PM _{2.5} head at a flow rate of 30 m ³ h ⁻¹	PM ₁ 150 mm-diameter quartz fibre filters using Digitel automatic high volume (30 m ³ hr ⁻¹) samplers.	PM _{2.5} PTFE filters using Partisol sampler (1 m ³ hr ⁻¹).	PM ₁₀ quartz filters sampled with a Digitel DHA-80 at 30 m ³ hr ⁻¹ during 24h. Filters preheated at 105°C.	PM ₁₀ Teflon filters sampled at 1 m ³ hr ⁻¹	PM _{2.5} Denuder – Teflon/Nylon filter pack sampled at 0.6 m ³ hr ⁻¹	PM ₁ filters quartz filters sampled with a Digitel DHA-80 at 30 m ³ hr ⁻¹ during 24h. Filters preheated at 105°C.	PM ₁₀ Quartz
Filter change time	09:00	00:00	08:00	00:00	00:00	07:00 19:00	09:00 21:00	00:00
Candidate method (CM)	PM ₁ ACSM	PM ₁ ACSM	PM ₁ HR-TOF-AMS	PM ₁₀ MARGA	PM ₁₀ MARGA	PM _{2.5} MARGA	PM ₁ MARGA	PM ₁₀ URG AIM
Reference	Bourin et al. (2019) ²⁶ Bourin et al (2020) ²⁷	Via, M. et al. (2021) ¹⁴	Ovadnevaite et al. (2014) ^{28,40}	Stieger et al. (2018) ⁷	Makkonen et al. (2012) ⁹	Rumsey et al. (2014) ⁸	Sandrini et al. (2016) ²⁹	Beccaceci et al. (2015) ¹⁰

188 Note: The EN16913:2017 only permits quartz filters for sampling.

189 **3. Results**

190 **3.1 Data capture**

191 The ACSM and the AIM met both the data coverage and time requirements of the Directive (Table 2 and Table 3 respectively).
 192 It is noted that in 2018 the AIM was only operated for the period between 01/01/2018 and 18/10/2018 at Marylebone Road.
 193 The MARGA (Table 4) also met the data coverage and time requirements of the Directive at Auchencorth Moss, whereas at
 194 the Chilbolton Observatory it was found that in 2017, K⁺ did not meet the data capture objective and in 2018 K⁺, Ca²⁺ and Mg²⁺
 195 did not meet the data capture objective. It is noted, that the MARGAs at both sites were replaced at the start of 2018 and low
 196 data capture is due to initial operational issues following the replacement of the instrument.

197

198 **Table 2** Data capture (hourly resolution) and number of days with > 90% data capture in 24 hours achieved at North
 199 Kensington, London for the PM₁ ACSM for the years 2016 to 2017. The directive target is 52 days per year. n/a:
 200 refractory species are not quantified by this method.

Species	Data capture (%)		# days	
	2016	2017	2016	2017
NH ₄ ⁺	55	75	168	243
Na ⁺	n/a	n/a	n/a	n/a
K ⁺	n/a	n/a	n/a	n/a
Ca ²⁺	n/a	n/a	n/a	n/a
Mg ²⁺	n/a	n/a	n/a	n/a
Cl ⁻	n/a	n/a	n/a	n/a
NO ₃ ⁻	55	75	168	243
SO ₄ ²⁻	55	75	168	243

201

202 **Table 3** Data capture (hourly resolution) and number of days with > 90% data capture in 24 hours at North Kensington (NK)
 203 and Marylebone Road (MR), London sites for the PM₁₀ AIM for the years 2016 to 2018 (data downloaded from UK-Air on
 204 the 09/11/2020). The directive target is 52 days per year. * Maximum number of days possible is 291 as instrument was
 205 only operational from 01/01/2018 to 18/10/2018 at North Kensington, London.

Species	Data capture (%)						# days					
	2016		2017		2018*		2016		2017		2018*	
	NK	MR	NK	MR	NK	MR	NK	MR	NK	MR	NK	MR
NH ₄ ⁺	70	63	77	44	53	67	224	188	239	122	133	207
Na ⁺	69	80	78	46	52	72	221	242	246	128	126	223
K ⁺	69	77	75	46	58	71	220	234	233	129	141	222
Ca ²⁺	62	70	79	45	58	72	198	210	248	126	143	224
Mg ²⁺	70	80	75	46	58	72	220	240	234	128	144	220
Cl ⁻	68	79	75	48	57	48	218	256	237	142	139	148
NO ₃ ⁻	69	80	76	48	61	48	218	258	239	142	150	149
SO ₄ ²⁻	68	77	71	46	57	48	219	247	225	139	240	149

206

207

208 **Table 4** Data capture (hourly resolution) and number of days with > 90% data capture in 24 hours at Auchencorth Moss
 209 (ACTH) and Chilbolton Observatory (CHBO) sites for the PM_{2.5} MARGA for the years 2016 to 2018 (data downloaded from
 210 UK-Air on the 09/11/2020). The directive target is 52 days per year. In bold are the times where the minimum number of
 211 days is not achieved in a year. * MARGA instrument replaced.

Species	Data capture (%)						# days					
	2016		2017		2018*		2016		2017		2018*	
	ACTH	CHBO	ACTH	CHBO	ACTH	CHBO	ACTH	CHBO	ACTH	CHBO	ACTH	CHBO
NH ₄ ⁺	63	54	52	81	73	65	193	176	128	270	202	169
Na ⁺	62	53	52	63	73	73	189	168	128	146	204	195
K ⁺	63	54	53	24	73	10	193	175	131	11	209	27
Ca ²⁺	61	54	55	81	74	8	184	176	137	271	211	20
Mg ²⁺	63	54	55	81	74	10	193	176	137	272	211	27
Cl ⁻	65	57	74	77	80	72	206	189	216	257	232	189
NO ₃ ⁻	65	57	74	78	80	73	206	189	216	264	232	195
SO ₄ ²⁻	65	57	74	77	80	73	206	188	216	258	232	197

212 3.2 Equivalence

213 Expanded uncertainty analysis was performed on each location individually, as large datasets, such as the MARGA Melpitz
 214 (Case study 4), were found to greatly influence the results when datasets from different case studies were combined. In addition,
 215 in the absence of standardised operating procedures, set-up varied (cut-off and sampling inlet length) between sites and
 216 therefore direct comparison cannot be made between case studies. All the calculated expanded uncertainties with the orthogonal
 217 regressions for each species can be found in the supplementary material (Figures S1 to S45).

218 3.2.1 ACSM and HR-TOF-AMS

219 Table 5 summarises the equivalence for the case studies #1 to #3 (Table 1) for the ACSM and HR-TOF-AMS. It was found
 220 that equivalence was possible for NH₄⁺, NO₃⁻ and SO₄²⁻, though either the slope or the slope and intercept required correction
 221 to meet the equivalence criteria. In the only study that reported chloride (Revin, Case Study 1, Figure S29), the ACSM failed
 222 to pass the expanded uncertainty criterion as expected. It is however noted that the reported concentrations were small (no Cl⁻
 223 > 2 µg m⁻³, Table 5) making the assessment on uncertainty challenging (RM mean = 0.122 µg m⁻³). In addition, the CM reported
 224 PM₁ compared to PM_{2.5} reported by the RM. It is likely that the RM contained sea salt and the ACSM is known to be unable to
 225 report Cl⁻ from sea salt as it is a refractory compound. For that reason, ACSM chloride data have not been processed any further
 226 in this study.
 227

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Table 5 Summary of equivalence for the ACSM and HR-TOF-AMS case studies. Highlighted in grey are where the expanded uncertainty (W_{cm}), slope or intercept fail the equivalence criteria. nssSO₄²⁻: non sea salt SO₄²⁻. Corrected - 2nd orthogonal regression was carried out to calculate the expanded uncertainty, after data had been calibrated (corrected) for either the slope (S), the intercept (I) or both (SI), based on the criteria outlined in Section 2.3.

Case study	Species	Raw						Corrected	
		Slope	Intercept	W_{cm} (%)	R^2	n	% > 2 $\mu\text{g m}^{-3}$	S,I or SI corrected	W_{cm} (%)
1	SO ₄ ²⁻	0.544	0.04	90	0.605	18	11	S	37
	NO ₃ ⁻	0.927	0.493	7	0.96	18	27.8	SI	16
	NH ₄ ⁺	0.742	0.201	47	0.949	18	11	SI	4
	Cl ⁻	-0.078	0.024	215.2	0.478	18	0	SI	132.5
2	SO ₄ ²⁻	1.092	-0.069	19	0.84	147	25.9	S	0.5
	NO ₃ ⁻	1.829	0.051	166	0.79	152	9.2	S	11.8
	NH ₄ ⁺	1.7	-0.119	138	0.75	152	2.6	SI	13.6
3	nssSO ₄ ²⁻	1.144	0.097	30.8	0.85	385	5.2	SI	2.3
	Total SO ₄ ²⁻	1.179	-0.045	34.9	0.84	384	5.5	SI	3.1
	NO ₃ ⁻	0.754	-0.111	51.5	0.83	334	6	SI	5.2
	NH ₄ ⁺	0.851	-0.002	30.0	0.85	348	2.9	S	2.7

233 3.2.2 MARGA

234 Table 6 summarises the performance of the MARGA instruments in Case Studies 4 to 7. It is immediately clear that no set-up
235 passed the W_{cm} criteria for all species but a combination of case studies provides evidence that the MARGA can pass the
236 equivalence criteria for each species.

237 At Melpitz (Case Study 4)⁷, Na⁺, K⁺ and Ca²⁺ failed the W_{cm} . Also, both Cl⁻ and NO₃⁻ still had a significant slope after
238 correction and therefore would not pass the equivalence test. Whereas at Kumpula (Case Study 5)⁹ only K⁺ failed to meet the
239 W_{cm} criteria of 50% even after correction, however there were only six data points and reported concentrations were low. In
240 the same study, Ca²⁺ and Mg²⁺ also failed to meet the equivalence criteria, due to the intercept still being significant for both,
241 as well as the slope for Mg²⁺, following correction.

242 For the Research Triangle Park site (Case Study 6), only NH₄⁺, NO₃⁻ and SO₄²⁻ data were available but the site operated 2
243 MARGAs (Case Studies 6a and 6b) in parallel against the RM of the US EPA⁸. A disadvantage of this study used a cut-off of
244 PM_{2.5} and the CM reported ~PM₂₆. As a result, NO₃⁻, which is typically found in both the coarse and fine fractions, had the
245 greatest uncertainty causing one instrument to fail the criterion (Table 6, Case Study 6a) with slopes ranging from 2.041 to
246 2.890 before correction. However, once the datasets were averaged and corrected the instrument passed the W_{cm} criterion (Case
247 Study 6c, Figure S14c). Ammonium also passed the criteria either as individual instruments or when averaged. For SO₄²⁻ either
248 as individual units or averaged both the intercept and slope correction was required to pass the W_{cm} .

249 In the final MARGA case study at San Pietro Capofiume (Case Study 7), NH₄⁺, NO₃⁻ and SO₄²⁻ passed the W_{cm} criterion
250 even though the CM reported consistently higher concentrations. Potassium also passed equivalence without correction, though
251 there is no significant correlation between the reported RM and CM ($R^2 = 0.161$). The poor relationship is likely to be due to
252 the low concentrations of ~0.05 $\mu\text{g m}^{-3}$, which are below the detection limits of the MARGA when the IC uses injection loops
253 rather than pre-concentrator columns that lower the detection limit (Table S1).
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Table 6 Summary of equivalence for the MARGA (case studies 4 to 7). Case study 6a (CM1) and 6b (CM2), are collocated MARGAs are the same station, whereas 6c is the combined MARGA datasets from the same station (CM1 and CM2). Highlighted in grey are where the expanded uncertainty, slope or intercept fail the equivalence criteria. Corrected - 2nd orthogonal regression was carried out to calculate the expanded uncertainty, after data had been calibrated (corrected) for either the slope (S), the intercept (I) or both (SI), based on the criteria outlined in Section 2.3. N/A – not applicable.

Case study	Species	Raw						Corrected		
		Slope	Intercept	W _{cm} (%)	R ²	n	% > 2 µg m ⁻³	S,I or SI corrected	W _{cm} (%)	S, I, or SI still significant following correction
4	Cl ⁻	0.648	0.079	69	0.852	710	2.5	SI	6.7	S
	SO ₄ ²⁻	0.826	0.016	35	0.907	1475	45	S	6.6	No
	NO ₃ ⁻	0.679	0.564	55	0.875	1488	55	SI	25	S
	NH ₄ ⁺	0.822	-0.100	38	0.865	1453	33	SI	2.4	No
	Mg ²⁺	0.731	0.061	53	0.587	109	0	SI	19	No
	Na ⁺	0.411	0.070	116	0.567	333	0	SI	53	SI
	K ⁺	0.563	0.024	87	0.414	151	0	SI	67	SI
	Ca ²⁺	2.829	-0.210	362	0.128	343	0	SI	146	SI
5	Cl ⁻	0.772	0.045	45	0.831	39	0	SI	4.9	No
	SO ₄ ²⁻	0.846	0.232	26	0.982	86	44.2	SI	0.2	No
	NO ₃ ⁻	0.930	0.413	5.7	0.935	84	25.0	SI	0.4	No
	NH ₄ ⁺	0.991	-0.374	9.2	0.822	74	9.5	I	1.7	No
	Mg ²⁺	3.957	-0.043	591	0.716	86	0	SI	49	SI
	Na ⁺	0.736	-0.089	55	0.608	35	0	SI	20	No
	K ⁺	-0.054	0.122	208	0.020	6	0	SI	8306	SI
	Ca ²⁺	3.505	0.027	502	0.846	81	0	S	29	I
6a	SO ₄ ²⁻	0.973	0.281	0.2	0.996	60	56.7	SI	0.2	No
	NH ₄ ⁺	1.031	0.028	6.8	0.972	60	3.3	N/A	N/A	No
	NO ₃ ⁻	2.890	-0.400	370	0.797	60	0	SI	52	No
6b	SO ₄ ²⁻	0.978	0.208	0.2	0.995	60	56.7	SI	0.2	No
	NH ₄ ⁺	0.986	0.079	1.2	0.960	60	3.3	I	2.75	No
	NO ₃ ⁻	2.041	-0.244	203	0.810	60	0	SI	27	No
6c	SO ₄ ²⁻	0.975	0.246	0.1	0.996	60	56.7	SI	0.1	No
	NH ₄ ⁺	1.007	0.054	2.6	0.969	60	3.3	I	1.5	No
	NO ₃ ⁻	2.447	-0.316	283	0.809	60	0	SI	37	No
7	Cl ⁻	3.903	0.14	584	0.492	29	0	SI	324	S
	SO ₄ ²⁻	0.946	0.539	0.1	0.856	29	55.2	I	11.0	No
	NO ₃ ⁻	1.214	0.489	52.6	0.95	29	34.5	SI	5.8	No
	NH ₄ ⁺	1.249	-0.059	48.7	0.922	26	19.2	S	10.3	No
	Mg ²⁺	21.680	-0.164	4134	0.003	23	0	SI	343	SI
	Na ⁺	3.371	-0.026	474	0.141	21	0	SI	310	SI
	K ⁺	1.032	-0.023	6.0	0.161	12	0	N/A	N/A	No
	Ca ²⁺	0.978	0.050	3.4	0.088	26	0	I	4.45	No

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263 3.2.3 AIM

264 The AIM at North Kensington (Case Study 8) passed the expanded uncertainty criteria for all species, with the exception of
 265 Na⁺, K⁺ and Ca²⁺ (Table 7). It was evident in studying the times series, ion balance and the theoretical concentration of sea salt
 266 (Figures S46 to 47) that Na⁺ was overestimated by the CM compared to the RM. This would explain why it failed to pass the
 267 expanded uncertainty. K⁺ was also overestimated compared to the RM and could not be corrected.
 268

269 **Table 7** Summary of equivalence for the AIM (Case Study 8). Highlighted in grey are where the expanded uncertainty, slope
 270 or intercept fail the equivalence criteria. Corrected - 2nd orthogonal regression was carried out to calculate the expanded
 271 uncertainty, after data had been calibrated (corrected) for either the slope (S), the intercept (I) or both (SI), based on the
 272 criteria outlined in Section 2.3.

Ion	Raw						Corrected		S, I, or SI still significant following correction
	Slope	Intercept	W _{cm} (%)	R ²	n	% >2μg m ⁻³	S,I or SI corrected	W _{cm} (%)	
Cl ⁻	0.585	0.439	74	0.901	32	25	SI	5	No
SO ₄ ²⁻	0.896	-0.226	26	0.931	33	27	S	4	No
NO ₃ ⁻	0.895	0.26	28	0.895	33	42	S	30	No
NH ₄ ⁺	1.493	0.439	105	0.890	33	18	SI	17	No
Mg ²⁺	0.934	0.001	13	0.963	33	0	S	0.3	No
Na ⁺	1.773	0.580	167	0.441	33	9.1	SI	58	S
K ⁺	52.347	-1.202	10246	0.003	33	0	SI	230	SI
Ca ²⁺	0.556	0.142	86	0.446	33	0	SI	61	No

273

274 **4. Discussion**

275 As previously discussed, (section 3.1) all three CMs met the data capture objectives, however, the expanded uncertainty
 276 criteria was not met for all species by all three CMs. Further discussion of this, and limitations associated with the candidate
 277 methods are provided in this section.

278 **4.1 Performance of the expanded uncertainty analysis**

279 For all case studies, the W_{cm} was passed for NH₄⁺ following corrections. However, the corrections required (slope and/or
 280 intercept) for the CMs were not consistent between case studies, which is true for all species studied. This is likely due to the
 281 varying set-ups and calibration strategies, as well as varying meteorological conditions and chemical regimes between case
 282 studies, as outlined in Table 1. The expanded uncertainty criterion for NO₃⁻ was passed by all except for the Melpitz data (Case
 283 Study 4), which still had a significant slope. Stieger et al. (2018)⁷ discussed the differences between filter and the MARGA for
 284 NO₃⁻ and concluded that in summer NH₄NO₃ is lost from filters through volatilisation, leading to an underestimation, whereas
 285 in winter the filter reports higher concentrations compared to the MARGA. To investigate this hypothesis of volatilisation from
 286 filters the San Pietro Capofiume data was studied (Case Study 7) as sampling was for 12 hours rather than 24 hours (Table 1,
 287 Figure 1). It was found that during the day NO₃⁻ had a large uncertainty (W_{cm} = 11362 %), as concentrations were low, whereas
 288 at night, when a larger concentration range was reported (Table 8), the uncertainty met the criteria (W_{cm} = 2.26). No relationship
 289 however could be found to link the reported concentration difference between the RM and CM to mean temperature, as it is a
 290 controlling mechanism of volatilisation losses from the filter. The effect however could be masked by the low daytime
 291 concentrations that were challenging the detection limits of the MARGA that was operating with injection loops (Table S1). It
 292 is however beyond the scope of this phase 1 study to investigate the influence of meteorology.

293 Sulfate was the third species reported by all CMs in the case studies. All studies met the W_{cm} criteria. For the ACSM case
 294 studies only the slope was required to be corrected, whereas the HR-TOF-AMS (Case Study 3) required correction of both the
 295 slope and the intercept. As the HR-TOF-AMS was based at the coastal site of Mace Head it is expected that total SO₄²⁻ reported

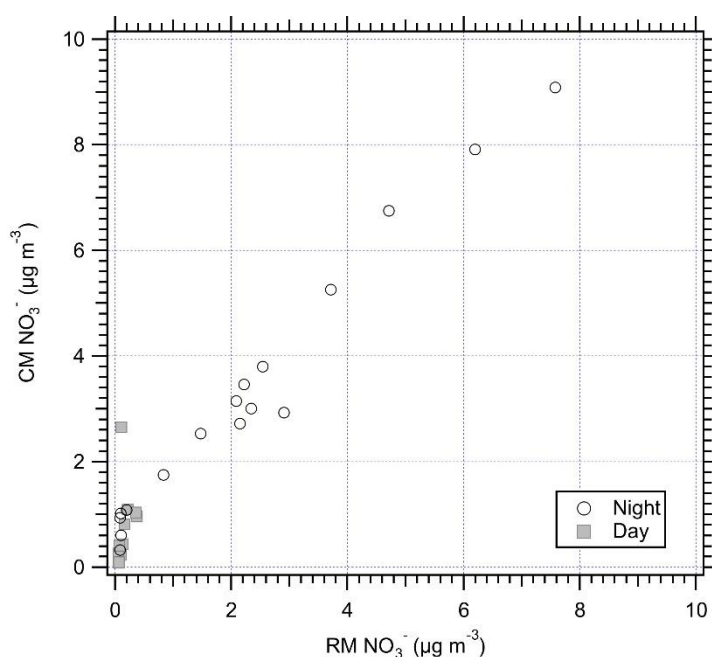
296 by the RM includes a significant fraction of sea salt SO_4^{2-} which cannot be detected by the HR-ToF-AMS due to its super-
297 micron size and refractory nature.

298 Out of the case studies using either the ACSM or the HR-TOF-AMS, only one case study provided chloride data as the other
299 studies had not calibrated their instruments for chloride. It was found in the study the ACSM failed the W_{cm} criteria (Revin,
300 Case Study 1), which is not unexpected since the ACSM is insensitive to NaCl as the majority cannot be flash vapourised at
301 600°C ^{28,30} and the Cl^- reported is thought mainly to be in the form of NH_4Cl . However there have been attempts to quantify
302 seasalt Cl^- from HR-TOF-AMS high resolution data by quantifying the degree of the incomplete vaporisation or the instrument
303 background signal^{31,32} therefore in a future equivalence study it is recommended that this possibility should be explored. The
304 MARGA at the San Pietro Capofiume (SPC) site (Case Study 7) also failed on Cl^- , whereas the other two MARGA case studies
305 passed (Case Studies 4 and 5). This is probably due to the difference in the ambient average concentration, where it was 0.02
306 $\mu\text{g m}^{-3}$ at SPC compared to $0.26 \mu\text{g m}^{-3}$ and $0.14 \mu\text{g m}^{-3}$ at Melpitz (Case study 4) and Kumpula (Case study 5), respectively.
307 The AIM (Case Study 8) also passed the W_{cm} criteria for Cl^- .

308 Only the two IC-based CMs (MARGA and AIM) are able to report base cations. Three of the datasets submitted for the
309 MARGA reported Na^+ , all of which were below $2 \mu\text{g m}^{-3}$ in concentration. The dataset from Kumpula (Case Study 5) passed
310 the expanded uncertainty criteria with an average reported concentration of $0.23 \mu\text{g m}^{-3}$, however the relationship was not
311 strong, with an $R^2 = 0.61$. The other two MARGA datasets did not pass (Case Studies 4 and 6). The AIM also did not pass the
312 expanded uncertainty criteria (Case Study 7), where the average reported concentration was $1.04 \mu\text{g m}^{-3}$. Beccaceci *et al.* (2015)
313 ¹⁰ discuss that the AIM may have suffered from contamination, which would explain the overestimated Na^+ concentrations.

314 For the remaining cations, K^+ , Ca^{2+} and Mg^{2+} , not all studies passed the expanded uncertainty criteria and performance was
315 variable for the ion chromatography CMs. Only the MARGA at the SPC site (Case Study 7) passed the criteria for equivalence
316 for K^+ out of the three MARGA case studies, which is surprising as SPC reported the lowest average concentration of $0.05 \mu\text{g m}^{-3}$,
317 while Melpitz (Case study 4) and the Kumpula (Case study 5) sites reported $0.12 \mu\text{g m}^{-3}$ and $0.08 \mu\text{g m}^{-3}$, respectively. The
318 AIM also failed to demonstrate equivalence; however, the average concentration of $0.03 \mu\text{g m}^{-3}$ was close to the instrument
319 detection limit. For Ca^{2+} , again it was only the SPC site in case study 7 that passed the expanded uncertainty criteria however
320 no relationship could be found when studying the correlation. The SPC site however failed to pass the equivalence criteria for
321 Mg^{2+} . Instead, it was the Melpitz (Case study 4) and Kumpula (Case study 5), as well as the AIM (Case study 8) that passed
322 the equivalence criteria for Mg^{2+} .

323



324

325 **Figure 1** Twelve-hour $\text{PM}_{10} \text{NO}_3^-$ measurements at the San Pietro Capofiume field site (Case Study 7) with a MARGA as the
326 CM, split into day and night.

327

328 **Table 8** W_{cm} of $PM_{10} NO_3^-$ at San Pietro Capofiume reported by the CM (MARGA) for the whole period and separated into to
 329 day and night. Highlighted in grey are where the expanded uncertainty, slope or intercept fail the equivalence criteria.
 330 Corrected - 2nd orthogonal regression was carried out to calculated the expanded uncertainty, after data had been
 331 calibrated (corrected) for either the intercept (I) or both (SI), based on the criteria outlined in Section 2.3

Ion	Raw						Corrected	
	Slope	Intercept	W_{cm} (%)	R^2	n	% > $2 \mu g m^{-3}$	S,I or SI corrected	W_{cm} (%)
all	1.214	0.489	52.64	0.95	29	34.5	SI	5.8
day	20.591	2.383	3881.19	0.154	12	0	SI	11362
night	1.011	0.123	16.39	0.882	10	30	I	2.26

332

333 4.2 Inlet set up

334 Under the EN12341:2014 standard³³ sampling has to be carried out by using an inert, non-corroding, electrically conducting
 335 material such as stainless steel, anodized aluminium or aluminium alloy and it should not have any bends to minimise loses of
 336 aerosols. All the CMs presented were not automatically provided with an inlet by the manufacturer and so the inlet set up varied
 337 between sites (Table 1). Only the URG AIM used an anodized aluminium inlet with a vertical sampling position, so there was
 338 no bend as prescribed by the standard. The other CMs (MARGA, ACSM, HR-TOF-AMS) however all have a horizontal
 339 sampling position and therefore an inlet bend is included in the set-ups presented, which is likely to lead to aerosol losses. The
 340 inlet of the MARGA is a compromise design also to measure trace gases NH_3 and HNO_3 that are considered 'sticky' and choice
 341 of inlet material is therefore challenging. Evidence from previous studies³⁴⁻³⁶ suggests that use of stainless steel or anodized
 342 aluminium, whilst minimising particle losses, would lead to adsorption losses of gases to the inlet walls. Therefore, MARGA
 343 inlets tend to be constructed of polytetrafluoroethylene (PTFE), perfluoroalkoxy (PFA) or polyethylene (PE), (see Table 1),
 344 with Teflon-coated size-selectors to minimise the losses of reactive gases. In the case studies presented there were no consistent
 345 lengths either but the EN12341:2014 standard stipulates that inlet length can be no more than 3 m. If the proposed CMs are to
 346 be considered in the future for the standard, then additional work would be required to establish a standard inlet design for the
 347 candidate methods.

348 4.3 Limitations of the candidate methods

349 The size cut-off of the ACSM (and HR-TOF-AMS) is controlled by the characteristics of the aerodynamic lenses that focus
 350 the particles during transfer into the vacuum. This is controlled by the vacuum aerodynamic diameter rather than the cut-off
 351 aerodynamic diameter, which is different in their dependencies on particle density. In the datasets presented, the ACSM
 352 instruments were equipped with the standard (PM_{10}) aerodynamic lens, but more recently a $PM_{2.5}$ lens was made available by
 353 the manufacturer. Most of the studies comparing ACSM to filters in literature are made using PM_{10} lenses and highlight the
 354 difficulties of comparing different size cut off instruments. The first $PM_{2.5}$ ACSM set-ups had some issues with consistency in
 355 detecting larger particles, but lately advances in the inlet design, the use of a lens with improved transmission efficiency and
 356 the use of a capture vaporizer in the instrument have largely solved the issues in the new generation instruments^{37,38}. It would
 357 therefore have to be investigated if the equivalence demonstrated was possible for the ACSM with a $PM_{2.5}$ lens too.

358 The estimate of total mass loading from the ACSM requires the knowledge of the collection efficiency (CE) for the
 359 instrument. The CE of the ACSM needs to be evaluated regularly for the instrument and can depend on the chemical
 360 composition and on the relative humidity of the sampled air³⁹. To reduce uncertainties on CE the air is sampled through a nafion
 361 drier placed in front of the ACSM/AMS inlet. This will decrease the relative humidity, which is measured by a RH sensor
 362 between the drier and the ACSM/AMS. The RH is maintained below 40% to avoid any influence on the CE evaluation. A
 363 typical technique used to validate the CE involves a comparison between a volume concentration obtained from the ACSM
 364 data using the compounds densities and a volume concentration derived from a co-located Scanning Mobility Particle Sizer
 365 (SMPS) spectrometer or from a nephelometer. However, the recent development of the aforementioned capture vaporizer with
 366 near unity CE is likely to reduce this uncertainty in the future. This is applicable to the ACSM, but is incompatible with the
 367 sizing of the HR-TOF-AMS.

368 The main issue in using the ACSM is that not all species covered by the Directive can be measured by this method, as only
 369 non-refractory compounds can be detected by the ACSM. Species like sodium chloride, sodium sulfate, sodium nitrate and the

370 dust/crustal components such as K^+ , Ca^{2+} and Mg^+ are not included in the aerosol mass loading provided by the instrument and
371 so to meet the objective would require the presence of additional monitoring equipment. It is however reported in the literature
372 that the HR-TOF-AMS has been used to derive NaCl from sea salt⁴⁰. This said, the ACSM or the HR-TOF-AMS additionally
373 provides a quantitative measure of organic aerosol mass with additional information that can be used for its source
374 apportionment.

375 In the absence of internationally agreed standard operating procedures (SOP) for MARGAs and related instruments,
376 implementations vary significantly, and this makes comparisons difficult to interpret and generalise. For example, in the case
377 studies for W_{cm} presented, the instrument set-ups are different compared to the MARGAs already used in routine monitoring
378 in the UK⁵ as the MARGA operated at Auchencorth Moss, a remote rural background site⁴¹, which was used for studying the
379 data capture (but not for the W_{cm} assessment due to the lack of a RM measurement), operates with pre-concentration columns
380 rather than injection loops to achieve lower detection limit (see Table S1). Similarly, whilst all the MARGAs in the studies
381 presented used a cation eluent based on nitric acid (HNO_3), the UK MARGA network the Auchencorth Moss uses
382 methanesulfonic acid (MSA) and the Chilbolton instrument p-toluenesulfonic acid instead, because a carry-over of HNO_3 and
383 artefact in the anion analysis for nitrate has been observed in some of the systems and had to be corrected for in the San Pietro
384 Capofiume data⁹. Therefore, investigations would be required to determine the impact of pre-concentration columns and cation
385 eluent on achieving equivalence, and if a common optimum SOP required.

386 For the post processing of chromatograms, the MARGA instrument operators in these studies would have likely been
387 provided with the reanalysis tool by Metrohm. The use of this tool can be challenging due to inconsistent integration of
388 chromatograms as demonstrated by Chen et al. (2017)⁴², who recommended the use of another reintegration software
389 (Chromeleon V7.3, Thermo Scientific, Dionex). The issue of inconsistent integration, however, is thought to be resolved in the
390 new model of MARGA (MARGA 2060), as it uses a new software (MagicIC Net, Metrohm) for the integration of
391 chromatograms.

392 The case studies presented to demonstrate equivalence all use an earlier model of the MARGA that is no longer commercially
393 available. There are to date no datasets available to demonstrate equivalence using the new MARGA 2060 model. In the 2060
394 model both the air flow rate and liquid flowrates have been reduced, as well as the WRD being shortened, to try and minimise
395 the liquid consumption. In addition, the mass flow controllers used in the earlier MARGA model, have been replaced by a
396 critical orifice. The use of the critical orifice raises concerns since the mass flow rate is determined by temperature and pressure
397 and controls the speed of the particles going through a cut-off. The inability of the flow rate to respond to changes in ambient
398 temperature and pressure to keep the volumetric flowrate at the size cut constant will likely result in changes in the reported
399 cut-off. Under the current configuration, the MARGA 2060 using a critical orifice would fail to meet the EN12341:2014
400 standard for the size cut-off of $PM_{2.5}$. The case studies, however, have demonstrated that even with a different size cut-off,
401 equivalence is still possible in many conditions (Case Study 6), at least for components that are dominated by the accumulation
402 mode, contained within PM_1 , $PM_{2.5}$ and PM_{10} . Further investigations would be required to determine if the 2060 model could
403 demonstrate equivalence.

404 The AIM is normally operated with a $PM_{2.5}$ cyclone. During the field test period in 2013 a size selective PM_{10} monitoring
405 head was in operation at North Kensington. Although the method show an overall good correlation for NO_3^- , SO_4^{2-} , Cl^- , NH_4^+
406 and Mg^{2+} there is poor correlation found for Na^+ , K^+ and Ca^{2+} . Beccaceci *et al.* (2015)¹⁰ outline possible explanations for the
407 differences including positive instrument bias due to contamination, efficiency of particle extraction and removal of gases, but
408 this will require further investigation.

409 4.4 Limitations of the EN16913:2017 standard

410 The objective of $PM_{2.5}$ chemical composition data under the EU Air Quality Directive (AQD) 2008/50/EC is to provide
411 information on the levels in the background, which is used to assess the potential contribution from long-range transport, to
412 support source apportionment analysis of the contributors to total $PM_{2.5}$, and for understanding the behaviour of specific PM
413 pollutants². Under the EN16913:2017 a 24-hour average is produced for each species, compared to the proposed CMs which
414 produce online results at a higher time resolution of 1 hour or better. The current EN16913:2017 standard of 24 hours makes
415 interpretation with regards to long-range transport and source apportionment challenging as atmospheric conditions change at
416 a higher temporal resolution. This is especially important for disentangling air quality events in near real time to determine
417 which aspects are from domestic (national) emissions and which are the result of long-range transport (imported). The current
418 EN16913:2017 standard makes it impossible to respond to air quality events in near real time as it has a delay in reporting due
419 to samples only being collected typically on a weekly frequency (though at some sites this delay can be up to 16 days), followed
420 by analysis offline in a laboratory. The advantage of the sub-daily resolution from potential CMs is that it provides additional
421 information on the temporal pattern of emissions and the thermodynamic effects on gas/aerosol partitioning.

422 The EN16913:2017 methodology may not accurately report atmospheric concentrations and acknowledges that up to 30%
423 losses of volatile compounds such as NH_4NO_3 can occur⁶. The losses experienced by the RM for $\text{PM}_{2.5}$ mass sampling makes
424 this imperfect measurement data less usable for the assessment of atmospheric chemistry and transport models or to constrain
425 emissions. Indeed, some equivalence datasets, such as the summer MARGA data from Melpitz, appear to have been affected
426 by this shortcoming of the RMs. Rather than attempting to match an imperfect method (RM), future work should also investigate
427 whether CMs can be artificially degraded through a simulation of the impact of the losses that would be encountered by the
428 RM, likely as a function of temperature and humidity.

429 Evidence suggests that the organic fraction of $\text{PM}_{2.5}$, not currently reported under the Directive may be of greatest concern
430 to human health for acute exposure to PM due to its oxidative potential⁴³, compared to the inorganic species covered by the
431 EN16913:2017 standard. As organic PM is complex, high temporal resolution measurements would facilitate identification of
432 the sources necessary to develop and monitor mitigation strategies.

433 *4.5 Other potential candidate methods*

434 There are other methods available, which could potentially report components of the EN16913:2017 standard. The UK now
435 operates in-situ X-ray fluorescence spectrometry (XRF) instruments (Xact 625 Ambient Metals Monitor, Cooper
436 Environmental Services) at its three UK NERC Urban Supersites, which is a non-destructive method to provide elemental
437 composition. The system is able to quantify 24 elements (Si, S, Cl, K, Ca, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, As, Se, Cd, Sn
438 Sb, Ba, Pt, Hg, Pb, Bi, Pd) including K and Ca, which are in the EN16913:2017 standard. Furger et al. (2017)⁴⁴ carried out a
439 comparison of daily PM_{10} filters against the XRF method. It was found that for K and Ca there was excellent correlation to the
440 daily average filters. Tremper et al. (2018)⁴⁵ also investigated the performance of the XRF both in the laboratory and in the
441 field. The study concluded that Ca and K compared well to filters in the field but there was a positive difference in the slopes
442 when compared to AMS or AIM (for Ca^{2+} , Cl^- , K^+ and SO_4^{2-}), which was attributed to the differences in size, volatility, and
443 water solubility of the PM measured. It is therefore recommended that any future work to demonstrate equivalence to
444 EN16913:2017 should include XRF method, also to assess whether the combination of ACSM and XRF could provide
445 equivalence for all compounds of interest.

447 *4.6 Requirements for a future equivalence study*

448 This study is the first systematic comparison between the EN16913:2017 reference method (or similar filter methods) and
449 potential CMs using existing and available datasets to determine if equivalence is possible. It is noted that the studies assessed
450 were in most cases not specifically set up to compare the methods with datasets being serendipitous. As a result, this is not a
451 specifically designed equivalence study, rather a first step which demonstrates the clear need for one. None of the CMs
452 presented here operated with a $\text{PM}_{2.5}$ cut-off (the AMS for this size fraction being a recent innovation) making evaluating
453 equivalence challenging, as size distribution varies between ions. Not all of the CMs have an internationally recognised standard
454 operating protocols (SOP) except for the ACSM, for which one was developed under the European Aerosol, Cloud, and Trace
455 Gases Research Infrastructures (ACTRIS, <https://www.actris-ecac.eu/pmc-non-refractory-organics-and-inorganics.html>). A
456 future equivalence study should be designed to follow the Guide to Demonstrate Equivalence (GDE)¹⁶.

458 A future equivalence study would have to ensure:

- 459 1. All set-ups are prescribed in order that datasets can be comparable, including operating with a $\text{PM}_{2.5}$ cut-off.
- 460 2. All CMs have a user-community agreed SOP including quality control and quality assurance methodology.
- 461 3. Both laboratory and field studies will be required to be undertaken to assess the uncertainty compared to the RM.
- 462 4. Uncertainties will need to be quantified for sampling efficiency, analyte selectivity, blanks, calibration, repeatability
463 and instrument drift both under laboratory conditions and in the field.
- 464 5. Comparability between RM and CM, as well as the 'between sample' uncertainty of the CM will need to be assessed
465 under field conditions.
- 466 6. GDE recommends 4 minimum comparison field studies should be undertaken covering different chemical and
467 meteorological regimes.

469 **5. Conclusions**

470 This desk study has provided initial evidence that the MARGA has the potential to demonstrate equivalence for all species
471 included in the EN16913:2017 standard, whereas the ACSM/HR-TOF-AMS has the potential to demonstrate equivalence for
472 NH_4^+ , NO_3^- and SO_4^{2-} . The AIM has demonstrated equivalence for NH_4^+ , NO_3^- , SO_4^{2-} , Cl^- , and Mg^{2+} , however further
473 investigations would be required to understand if under optimised conditions, the AIM was possible for Na^+ , K^+ and Ca^{2+} to
474 pass the equivalence criteria.

475 There are operational differences between MARGA instruments including cation eluents, pre-concentration columns, and
476 inlet set-up; thus further investigations would be required to determine if this alters the potential for equivalence. This study
477 also did not include XRF spectrometry instruments. It is recommended to include XRF in any future equivalence study, which
478 could be a good complement to the ACSM, which returned promising results for SO_4^{2-} , NH_4^+ and NO_3^- , but cannot measure
479 base cations or the full suite of chloride compounds.

480 None of the case studies presented operated with a $\text{PM}_{2.5}$ cut-off for the candidate method and therefore further investigations
481 are required to confirm the above conclusions. It is therefore recommended that the next stage to undertake consists of targeted
482 laboratory and field studies of the CMs with the $\text{PM}_{2.5}$ cut-offs compared to the EN16913:2017 standard to demonstrate
483 equivalence.

484 Acknowledgements

485 The authors would like to thank the UK Environment Agency who funded this study.

486 The measurements in this study were funded by the following bodies:

- 487
- 488 - All the UK datasets were funded by UK Environment Agency under the UK Eutrophying and Acidifying Pollutant
489 Network and the UKs Particle Numbers and Concentrations Network. The Auchencorth Moss measurements are
490 supported by NERC UK Status, change and Projections of the Environment UK-SCaPE (NE/R016429/1).
 - 491 - The Revin fieldsite is coordinated by IMT Nord Europe in collaboration with the regional monitoring network (Atmo
492 Grand-Est) and the National Reference Laboratory for Air Quality Monitoring (LCSQA) and funded by the French
493 Ministry of Environment. ACSM measurements were supported by the Labex CaPPA project, which is funded by the
494 French National Research Agency (ANR) through the PIA (Programme d'Investissement d'Avenir) under contract
495 ANR-11-LABX-0005-01, and were part of the COST COLOSSAL Action CA16109.
 - 496 - Measurements in Barcelona Palau Reial were funded by the Spanish Ministry of Science and Innovation through CAIAC
497 project (PID2019-108990RB-I00) and FEDER funds, through EQC2018-004598-P.
 - 498 - Measurements at the Mace Head Atmospheric Research Station are supported by the EPA-Ireland and the Department
499 of Environment, Climate and Communications.
 - 500 - The Germany Federal Environment Agency (UBA) provided the financial support of this study and the deployment of
501 the MARGA at the research station Melpitz under contracts No: 351 01 093 and 351 01 070.
 - 502 - The data from Kumpula was supported by the Academy of Finland as part of the Centre of Excellence program (project
503 no 1118615).
 - 504 - US EPA gratefully acknowledges the contributions of Battelle and Wood (formerly Amec, Foster Wheeler) to the
505 Research Triangle Park study.
 - 506 - The data from the San Pietro Capofiume was funded by the PEGASOS EU FP7 project.

507 Data availability

508 The UK datasets are available on the DEFRA UK-Air (<https://uk-air.defra.gov.uk/>). Auchencorth Moss and Chilbolton
509 Observatory, UK datasets are also available on EBAS (<http://ebas.nilu.no/>). Data from Barcelona can be accessed here:
510 <https://doi.org/10.17632/xfv7z6jzcm.1>. The other datasets are available from the authors upon request.

511 Disclaimer

512 The views expressed in this article are those of the authors and do not necessarily represent the views or policies of the US
513 Environmental Protection Agency. Mention of trade names or commercial products does not constitute endorsement or
514 recommendation of use by the Agency.

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