Development of airborne particulate matter reference materials for chemical measurements and long-term monitoring of environmental changes

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Introduction

• Background

- Airborne particulate matter (PM) has drawn significant attention due to its detrimental effects on the environment and human health.
- Exposure to PM is associated with adverse health outcomes, including respiratory and cardiovascular diseases, and has recently been implicated in neurodegenerative diseases.
- The toxicity of PM is influenced not only by its size but also by the hazardous chemicals it contains.
- Understanding the composition of these chemicals can provide insights into the origins and growth mechanisms of PM.
- Given the complexity of PM samples, accurate chemical measurement is challenging, necessitating the development of certified reference materials (CRMs) for method validation and quality control.

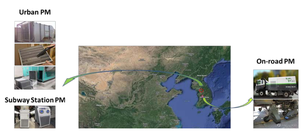
• Objective

- Development of PM CRMs for various chemical analysis, assessment of PM-mediated toxicity, source identification, and other basic researches
- Four CRMs under development: KRISS 109-02-004 (Urban PM), KRISS 109-02-005 (Subway station PM), KRISS 109-02-006 (On-road PM), KRISS 109-02-008 (Urban PM, 2nd batch for elemental analysis)
- Analytes of interest: Elements (geological/hazardous), POPs (PAHs), Water soluble ions (anions), Isotope ratios (C/N/S/Pb), Total carbon, Biologicals (bacteria, fungi, etc), Micro/nano plastics

Materials & Methods

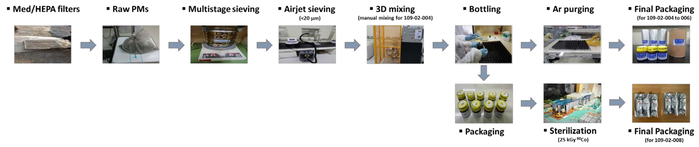
• Raw Materials

- **Large scale collection of raw materials**
  - KRISS 109-02-004 Urban PM: PM collected from intake-air filters of large buildings in the Greater Seoul area (5.6 kg) & air-purifier filters in subway stations in Seoul (0.6 kg) during 2019-2020
  - KRISS 109-02-005 Subway station PM: PM collected in air-purifier filters in subway stations in Seoul (6.6 kg) during 2021
  - KRISS 109-02-006 On-road PM: PM collected using road-dust suction vehicle in Daejeon (33 kg) for 1 day
  - KRISS 109-02-008 Urban PM (2nd batch): PM collected only from intake-air filters of large buildings in the Greater Seoul area (4.0 kg) during 2022-2023



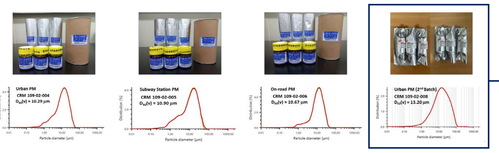
• Material Processing

- Each bottle contains more than 2 g PM samples.
- PM CRMs are stored at 4 °C, except for KRISS 109-02-008 2nd batch urban PM CRM (stored at room temp).

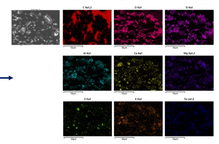


• Particle Characteristics

- **Particle size distribution:** Anton Parr PSA 1090LD



- **Particle morphology mapping using SEM-EDS:** Hitachi Regulus 8230



• Methods for Characterization

Elements

- Sample preparation: Microwave-assisted acid digestion with HNO_3 + HF
- Measurement method: **exact matching ID ICPMS** (high resolution SF ICPMS & triple Q-ICPMS), alternatively, **instrumental neutron activation analysis (INAA)** method used with **standard comparator calibration** for several elements. (Multielement analysis: k_0-**INAA** method)
- Homogeneity & reproducibility assessments

Water Soluble Anions

- Sample preparation: Ultrasonic extraction with water
- Measurement method: **ion chromatography (IC) with gravimetric standard addition** using bromide as internal standards
- Homogeneity & long-/short-term stability assessments

PAHs

- Sample preparation: Accelerated solvent extraction (ASE) with dichloromethane
- Measurement method: **exact matching ID GC-MS** (high resolution GC-MS)
- Homogeneity & long-/short-term stability assessments

Pb Isotope Ratio Deltas

- Sample preparation: : Microwave-assisted acid digestion using HNO_3 + HF, followed by H_3BO_3. Fractionation of Pb using Eichrom Sr resin.
- Measurement method: **Multi-collector ICPMS** measurement using **combined-standard sample bracketing with internal normalization (C-SSBIN)**: SRM 981 Pb & SRM 997 Tl.
- Homogeneity & stability assessments

C/N/S Isotope Ratio Deltas

- Sample preparation & measurement method: simultaneous analysis of C/N/S isotope ratio delta values using **elemental analyzer-isotope ratio mass spectrometry (EA-IRMS) with** multipoint calibration by isotope ratio references with different delta values [1]
- Homogeneity & stability assessments

Total Carbon

- NIOSH & IMPROVE protocols[2,3] were used and compared.
- Purity assessed glucose was used as a traceable primary standard for calibration of carbon analyzer.
- Homogeneity & long-term stability assessments

Results

• Elements

- KRISS PM CRMs: Significantly less amounts of hazardous elements (Pb, Cd, As, Hg) compared with those in NIST SRM 1648a collected in 1970s.
- Minimum sampling amounts: 10 mg for ID ICPMS, 50 mg for INAA

• Anions

- KRISS PM CRMs: Naturally occurring anions were characterized
- Minimum sampling amounts: 50 mg

• PAHs

- KRISS PM CRMs: Significantly less amounts of PAHs compared with those in NIST SRM 1648a collected in 1970s.
- Minimum sampling amounts: 150 mg

• Pb/C/N/S isotope ratio deltas

- KRISS 109-02-004 Urban PM CRM: First PM CRM with isotope ratio delta characterized.
- Pb & C isotope ratio deltas determine with *U* less than 1 %, but those for N & S were 8 & 51 %, respectively.
- Minimum sampling amounts: 20 mg for Pb, 5 mg for C/N/S

• Total carbon

- KRISS PM CRMs: TC similar to NIST SRM 1648a
- Minimum sampling amounts: 0.3 mg

• Multielement analysis by k_0-INAA (JSI)

- More than 40 elements analyzed
- QC sample (NIST SRM 1648a): $|E_n| < 1$ except for Ce, Mg, Sr, which are due to spectral interferences) & Ag, La, Se, W (Ref. Value)

• Microbiome analysis

- KRISS 109-02-005 Subway Station PM CRM: bacterial & fungal gene profiles, and relative abundances investigated [4].
- Homogeneity assessed. Stabilities at 4 °C, -20 °C, and -80 °C storage conditions are under investigation.
- Minimum sampling amounts: 2 g

• Micro-/nano-plastic analysis

- KRISS PM CRMs: higher amounts of micro-/nano-plastics than those in NIST SRM 1648a (manuscript in preparation)

Characterization Results (mg/kg); Draft data for 109-02-005 & 109-02-006, * INAA

Elements	NIST SRM1648a urban PM (certificate)	KRISS CRM 109-02-004 urban PM	KRISS CRM 109-02-005 subway station PM	KRISS CRM 109-02-006 on-road PM
Antimony (Sb)	45.4 ± 1.4	67.9 ± 3.0 (k=2.1)	42.97 ± 0.66 (k=2.0)	22.20 ± 0.62 (k=2.1)
Calcium (Ca)	58400 ± 1900	39500 ± 2400 (k=2.1)	25050 ± 350 (k=2.0)	34500 ± 420 (k=2.0)
Cobalt (Co)	17.93 ± 0.68	*19.96 ± 0.70 (k=2.2)	*23.08 ± 1.13 (k=2.2)	
Copper (Cu)	610 ± 70	4010 ± 300 (k=2.2)	23950 ± 340 (k=2.0)	202.6 ± 5.0 (k=2.1)
Chromium (Cr)	402 ± 13	*307 ± 14 (k=2.2)	*773.4 ± 31.6 (k=2.2)	
Iron (Fe)	39200 ± 2100			28890 ± 770 (k=2.0)
Lead (Pb)	6550 ± 330	293 ± 13 (k=2.1)	104.5 ± 2.2 (k=2.1)	68.9 ± 4.0 (k=2.0)
Magnesium (Mg)	8130 ± 120	9430 ± 540 (k=2.1)	4505 ± 58 (k=2.0)	7980 ± 160 (k=2.1)
Nickel (Ni)	81.1 ± 6.8	-	280.4 ± 3.0 (k=2.0)	34.2 ± 1.4 (k=2.1)
Potassium (K)	10560 ± 490			15540 ± 240 (k=2.0)
Tin (Sn)		191 ± 12 (k=2.2)	645 ± 14 (k=2.0)	45.6 ± 1.7 (k=2.1)
Zinc (Zn)	4800 ± 270	8170 ± 440 (k=2.1)	1943 ± 35 (k=2.0)	1189 ± 18 (k=2.0)
Zinc (Zn)		*8250 ± 320 (k=2.1)	*1947 ± 88 (k=2.1)	

Certified values (mg/kg): officialization required

Anions	NIST SRM1648a Urban PM (certificate)	KRISS CRM 109-02-004 urban PM	KRISS CRM 109-02-005 subway station PM	KRISS CRM 109-02-006 on-road PM
Fluoride	NA	348 ± 42 (k=2.2)	157 ± 25 (k=2.3)	< 80
Chloride	NA	7440 ± 410 (k=2.2)	5570 ± 610 (k=2.3)	185300 ± 1300 (k=2.2)
Nitrate	NA	54400 ± 2500 (k=2.2)	28240 ± 400 (k=2.3)	< 500
Sulfate	NA	44900 ± 2500 (k=2.2)	12640 ± 120 (k=2.3)	6002 ± 99 (k=2.2)

Certified values (mg/kg): officialization required

	PAHs	NIST SRM1648a Urban PM (certificate)	KRISS CRM 109-02-004 urban PM	KRISS CRM 109-02-005 subway station PM	KRISS CRM 109-02-006 on-road PM
1	Benz[a]anthracene	2.71 ± 0.15	0.494 ± 0.046 (k=2.2)	0.685 ± 0.046 (k=2.2)	0.181 ± 0.010 (k=2.5)
2	Triphenylene	2.04 ± 0.13	0.399 ± 0.039 (k=2.2)	0.595 ± 0.041 (k=2.2)	0.135 ± 0.010 (k=2.2)
3	Chrysene	6.12 ± 0.06	1.019 ± 0.097 (k=2.2)	1.56 ± 0.11 (k=2.2)	0.290 ± 0.014 (k=2.2)
4	Benzo(b)fluoranthene	8.89 ± 0.05	1.24 ± 0.12 (k=2.2)	1.067 ± 0.086 (k=2.2)	0.245 ± 0.011 (k=2.1)
5	Benzo(k)fluoranthene	3.03 ± 0.24	0.420 ± 0.045 (k=2.1)	0.357 ± 0.035 (k=2.2)	0.093 ± 0.007 (k=2.1)
6	Benzo(j)fluoranthene	3.20 ± 0.03	0.466 ± 0.046 (k=2.2)	0.379 ± 0.032 (k=2.2)	0.095 ± 0.005 (k=2.1)
7	Benzo(e)pyrene	4.85 ± 0.07	0.89 ± 0.10 (k=2.2)	0.566 ± 0.049 (k=2.2)	0.381 ± 0.016 (k=2.6)
8	Benzo(a)pyrene	2.57 ± 0.10	0.354 ± 0.032 (k=2.2)	0.153 ± 0.025 (k=2.2)	0.316 ± 0.014 (k=2.1)
9	Indeno(1,2,3-cd)pyrene	4.17 ± 0.17	0.742 ± 0.087 (k=2.2)	0.310 ± 0.050 (k=2.2)	0.335 ± 0.016 (k=2.1)
10	Benzo(g,h,i)perylene	5.00 ± 0.18	1.11 ± 0.12 (k=2.2)	0.366 ± 0.054 (k=2.2)	1.257 ± 0.092 (k=2.2)

Pb Isotope Ratio Delta (‰)

CRM	δ(206/204Pb)	δ(207/204Pb)	δ(208/204Pb)	δ(208/206Pb)
109-02-004	59.775 ± 0.12 (k=2.2)	7.464 ± 0.040 (k=2.2)	38.303 ± 0.086 (k=2.2)	-20.260 ± 0.11 (k=2.2)

C/N/S Isotope Ratio Delta (‰)

CRM	$\delta^{13}C_{VPDB}$	$\delta^{15}N_{air\text{-}N_2}$	$\delta^{34}S_{VCDT}$
109-02-004	-24.97 ± 0.16 (k=2.0)	5.47 ± 0.44 (k=2.0)	4.94 ± 2.50 (k=2.0)

Total Carbon (g/g): Draft data for 109-02-004, 109-02-005, and 109-02-006 (need dry-mass correction)

Protocols	NIST SRM1648a Urban PM (certificate)	KRISS CRM 109-02-004 urban PM	KRISS CRM 109-02-005 subway station PM	KRISS CRM 109-02-006 on-road PM
NIOSH[2,3]	0.127	0.1210 ± 0.0052 (k=2.0)	0.1223 ± 0.0039 (k=2.0)	0.0977 ± 0.0031 (k=2.0)
IMPROVE[3]		0.1230 ± 0.0039 (k=2.0)		

	NIST SRM 1648a					Urban PM			Subway station PM			On-road PM		
	NIST values		k0-INAA			k0-INAA			k0-INAA			k0-INAA		
	Mass Fraction, mg/kg	Expanded Uncertainty, mg/kg (k=2)	Mass Fraction, mg/kg	Expanded Uncertainty, mg/kg (k=2)	En-score (k=2)	Mass Fraction, mg/kg	Expanded Uncertainty, mg/kg (k=2)	diff. urban /NIST	Mass Fraction, mg/kg	Expanded Uncertainty, mg/kg (k=2)	diff. subway /urban	Mass Fraction, mg/kg	Expanded Uncertainty, mg/kg (k=2)	diff. road /urban
Ag	4.0	0.3	7.09	0.59	1.66	1.68	0.27	-78%	3.11	0.22	85%			
Al	34300	1300	33423	2708	-0.29	50042	3726	50%	16892	1206	-66%	46120	3462	-7.8%
As	115.5	3.9	123.2	10.0	0.72	61.7	4.4	-50%	27.56	1.97	-55%	8.20	0.59	-87%
Au			0.0430	0.0036	-									
Ba			752	63	-	2437	188	224%	3317	232	36%	797	59	-67%
Br	502	10	505	39	0.07	47.1	3.3	-91%	29.4	2.1	-38%	39.3	2.8	-17%
Ca	58400	1900	56072	4652	-0.46	37261	2952	-34%	23530	1968	-37%	30519	2172	-18%
Cd	73.7	2.3	76.5	6.2	0.42									
Ce	54.5	2.2	48.2	3.9	-1.42	65.10	4.62	35%	21.11	1.70	-68%	54.5	4.0	-16%
Cl	4543	47	4655	383	0.29	8109	580	74%	7492	551	-7.6%	183137	12986	2158%
Co	17.93	0.68	16.80	1.36	-0.74	19.38	1.37	15%	22.37	1.57	15%	9.19	0.66	-53%
Cr	402	13	385	31	-0.51	301	21	-22%	755	53	151%	95.8	7.1	-68%
Cs	3.4	0.2	3.48	0.28	0.22	5.074	0.358	46%	1.704	0.120	-66%	3.86	0.28	-24%
Cu	610	70	640	100	0.24	4150	321	549%	24328	1776	486%			
Dy			3.09	0.35	-									
Eu			0.862	0.054	-	0.962	0.069	45%	0.325	0.023	-66%	0.691	0.049	-28%
Fe	39200	2100	36756	2974	-0.67	89705	6287	144%	341363	23934	281%	27261	1940	-70%
Gd					-							3.64	0.54	
Hf	5.2	-	4.01	0.33	-	9.37	0.67	134%	28.20	1.98	201%	5.16	0.39	-45%
Hg	1.323	0.064	1.24	0.18	-0.44									
I			16.3	2.7	-	27.9	4.0	71%						
In			1.038	0.092	-	1.309	0.102	26%						
K	10560	490	9904	886	-0.65	16025	1575	62%	6241	559	-61%	16775	2298	4.7%
La	39	3	33.9	2.7	-1.25	35.2	2.5	3.9%	13.38	1.08	-62%	26.48	1.93	-25%
Lu			0.290	0.025	-	0.302	0.023	4.2%	0.2364	0.0168	-22%	0.2305	0.0165	-24%
Mg	8130	120	7187	835	-1.12	10560	969	47%	5036	484	-52%	8075	682	-24%
Mn	790	44	792	64	0.03	1110	80	40%	3441	241	210%	435	31	-61%
Mo			17.08	1.42	-	71.0	5.0	315%	330	23	365%	10.13	0.81	-86%
Na	4240	60	4200	320	-0.12	13645	969	225%	5250	371	-62%	117694	8483	763%
Nd			25.4	2.2	-	25.24	1.95	-0.5%				22.35	1.64	-11%
Ni	81.1	6.8			-									
Rb	51.0	1.5	47.3	4.1	-0.85	87.0	6.5	84%	32.2	2.8	-63%	85.9	6.3	-1.3%
S	55100	3600			-									
Sb	45.4	1.4	44.9	3.6	-0.14	67.9	4.8	51%	43.7	3.1	-36%	22.09	1.61	-67%
Sc	6 to 120	-	6.28	0.51	-	7.53	0.53	20%	2.811	0.198	-63%	5.40	0.39	-28%
Se	28.4	1.1	24.53	1.99	-1.70	8.83	0.75	-64%	2.93	0.33	-67%		0.00	
Sm	4.3	0.3	4.18	0.34	-0.27	4.50	0.32	7.7%	1.446	0.103	-68%	3.78	0.28	-16%
Sn			145	19	-	193	24	33%	647	47	236%			
Sr	215	17	247	26	1.03							211.1	18.8	
Ta			6.37	0.52	-	0.984	0.075	-85%	0.286	0.022	-71%	1.056	0.080	7.3%
Tb			0.500	0.042	-	0.806	0.058	61%	0.280	0.021	-65%	0.511	0.038	-37%
Th	7 to 107	-	7.05	0.57	-	12.35	0.88	75%	4.25	0.31	-66%	10.46	0.77	-15%
Ti	4021	86	3945	396	-0.19	3384	244	-14%	1521	317	-55%	3313	294	-2.1%
U			5.50	0.45	-	2.94	0.21	-47%	1.712	0.121	-42%	3.25	0.23	11%
V	127	11	132	11	0.31	76.1	5.7	-42%	65.7	4.9	-14%	47.2	5.8	-38%
W	4.6	0.3	5.51	0.54	1.48	37.9	2.7	588%	26.96	1.90	-29%		0.00	
Yb			1.709	0.143	-	1.789	0.132	4.6%	1.210	0.101	-32%	1.407	0.099	-21%
Zn	4800	270	4474	362	-0.72	8107	568	81%	1894	133	-77%	1115	79	-86%
Zr			170	22	-	402	43	137%	1292	92	221%	217.1	17.0	-46%
	ref. value													
	info. value													

Conclusions

- Three KRISS PM CRMs, reflecting the current atmospheric environment in Korea, have been developed.
- Two additional PM CRMs including a filter-type CRM are under development.
- These PM CRMs are valuable tools for method validation & quality control in the chemical analysis of airborne particulate matter.
- The characterized properties and their combinations can provide useful insights for source identification & fundamental research.
- The development of reference materials for analytes lacking metrological traceability, such as micro/nano-plastics & microbiomes, remains essential for harmonizing complex measurements.
- Characterizing the vast number of organic pollutants, including various PFAS & POPs, in PM CRMs continues to pose significant challenges.

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