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Subject Change in the analytical protocol for XRF analysis

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Supporting information

The element content of collected IMPROVE samples is quantified by energy-dispersive x-ray fluorescence (EDXRF) analysis. The instruments used since the 2011 sample year employ a primary x-ray tube to excite a sequence of secondary targets, whose secondary excitation spectra in turn irradiate the sample. Different targets yield different secondary spectra, preferentially exciting fluorescence from different elements in the sample. The sequence of secondary targets is chosen to optimize the resolution of important sample elements.

In order to improve detection of lead and some other elements, the analytical protocol for XRF analysis was slightly modified starting with samples collected in October 2018. The KBr secondary target, previously included to highlight arsenic, was dropped to allow more time for some of the other targets in the sequence (see table below). Longer target irradiation generally improves sensitivities for the elements reported from that target. The effects on data quality are expected to be small, detectable only after a sufficient record has been acquired with the new protocol. The XRF analyzers have now been recalibrated with the modified protocol, and all IMPROVE samples starting October 2018 are being reported with the new calibration and new analytical protocol.

Sample Element	Secondary Target	Exposure (sec), Old	Exposure (sec), New
Na – K	CaF ₂	600	600
Ca – Cr	Fe	400	400
Mn - Zn	Ge	300	400
As	KBr	300	
Se – Br	SrF ₂	300	
As– Br	SrF ₂		400
Rb – Sr, Pb	Мо	300	400
Zr	Al ₂ O ₃	200	200

Table. EDXRF protocols for samples collected before and after the beginning of October 2018.