A NOVEL METHOD FOR COMBINED Pb, Zn and Cu ISOTOPE RATIO DETERMINATIONS IN AEROSOL SAMPLES AND MAN-MADE MATERIALS: IMPLICATIONS ON ATMOSPHERIC POLLUTION TRACING

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The application of multiple isotope systems in aerosol samples enables unparalleled insights into sources and trace dispersion pathways of metal on the atmosphere. However, multi-isotope analyses in aerosol samples are difficult due to sample size limitation and low mass and elemental concentrations of the target elements, not to mention the laborious combination of individual ion exchange procedures for the different metals. To address this challenge, we developed and validated a novel method for the combined analysis of Pb, Cu and Zn isotope ratios in atmospheric aerosols. The method was applied in aerosol samples from São Paulo megacity in order to trace air pollutant sources. The method encompasses a new ion exchange chromatographic sequential separation protocol and we present instrumental measurements investigation regarding the mass-bias effects using MC-ICP-MS (Multi Collector Inductively Coupled Plasma Mass Spectrometry) for Cu and Zn isotopes. Lead isotopes were analyzed using TIMS (Thermal Ionizaton Mass Spectrometry). Validation was carried using Reference Materials (RM) and main urban pollutant sources (cement, road dust and tires). Purification efficiency and element recovery of the combined separation procedure were determined using the BCR-2 RM and an aerosol sample. Accuracy of our methodology was assessed with RMs analysis (BHVO, BCR, AGV, San Joaquin-2709, Sediment-1646a, Tomatoes-1573a), which agreed with reported data from other laboratories. The combined precision obtained for RMs and unknown samples (aerosol, tyre, road dust and cement) was 0.1‰ for $\delta^{66}Zn_{JMC}$ values, 0.13‰ for $\delta^{65}Cu_{NIST}$ values, and 0.035 for $^{206}Pb/^{204}Pb$ ratios. Lead, copper and zinc isotope compositions in urban aerosol from the São Paulo megacity showed a significantly range of values: between 1.170 and 1.250 for $^{206}Pb/^{207}Pb$ ratios, from 0.18 to 0.95‰ for $\delta^{66}Zn_{JMC}$ values, and between 0.12 and 0.60‰ for $\delta^{65}Cu_{NIST}$ values. The combined information of Pb, Cu and Zn isotopes allowed discriminating different air pollutant sources: Zn isotopes discriminated road dust and tires ($\delta^{66}Zn_{JMC} > 0.12$‰) from gasoline exhaust ($\delta^{66}Zn_{JMC} <$ -0.1‰), Cu isotopes differentiated road dust ($\delta^{65}Cu_{NIST}$ 0.04 ± 0.04‰) from cement ($\delta^{65}Cu_{NIST}$ 0.41 ± 0.10‰), whereas Pb isotopes distinguished vehicular traffic, road dust and tires ($^{206}Pb/^{207}Pb < 1.19$) from industrial area ($^{206}Pb/^{207}Pb > 1.22$). These results

provide a stepping-stone to further evaluate the use combined of Pb, Cu and Zn isotopes as tracers in urban atmospheric environments.