Direct determination of uranium, thorium and lead isotopes ratios in crude oils by fs-LA-ICP-MS.

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Estimation of crude oil expulsion timing from the rock source has important implications for the modeling of petroleum systems. Moreover, trace metal quantification in organic matrices (oil-to-oil correlation, oil-to-source correlation, biodegradation, migration,…) represents a challenge for organic geochemistry.

A new analytical approach using a high repetition rate IR-femtosecond laser coupled to an ICP-MS detection was developed. This technique allows the direct determination of trace elements in crude oil without sample preparation. Limits of detection are obtained at the ppb level in pure petroleum matrices.

The study of Uranium, Thorium and Lead isotopes in petroleum matrices by fs-LA-ICP-MS gave two important informations:

(1) Crude oils are very poor in Uranium and Thorium (concentration < 1 ppb) compare to Lead (10 ppb – 10 ppm) i.e. very low U/Pb and Th/Pb ratios. So the determination of crude oil expulsion time is hardly realizable with classical U/Th/Pb isochrones, but needs the comparison between lead isotopes ratios obtained from source rocks and crude oils. Indeed, the crude oil fixes the lead isotope signature of the expulsion time.

(2) Lead isotopic ratios trace clearly a mantle contribution. Therefore, they can discriminate 3 end-members: mantle lead, crustal lead, and anthropic contamination.

Hourly-size segregated sampling of trace elements and subsequent source apportionment

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Measurements of trace element concentrations in ambient aerosol were conducted at different sites (urban and rural) with the objective to apply source apportionment analysis.

Sampling was performed in three size ranges (0.1-1, 1-2.5 and 2.5-10 µm) with a rotating drum impactor (RDI). Samples were subsequently analyzed with synchrotron radiation X-ray fluorescence spectroscopy (SR-XRF) which allows for the detection of low mass concentrations (a few ng/m^3). For SR-XRF the sampling time can be significantly reduced compared to wet-chemical and conventional filter analysis and the investigation of diurnal variations becomes feasible. XRF-analysis at different incident energies lead to a range of detected elements from Al – Zn, resp. Ba.

Although trace elements do not appear in high concentrations they can provide indications about the origin of different kinds of air pollution (e.g. traffic, wood burning, mineral dust etc). Without a-priori knowledge about the sources positive matrix factorisation (PMF) was employed to mimic their contribution as well as their time evolution. For 0.1-1 µm particles one typical factor is wood burning showing contributions of sulphur, potassium, calcium and zinc. Furthermore there is a fraction related to soil and terrestrial elements, and a single peak of sulphur presumably representing secondary sulphate. Another factor leads to the assumption of a vehicle/traffic related exhaust/abrasion source. The final goal is to combine for the first time the RDI-SR-XRF data set with aerosol mass spectrometer (AMS) data, providing information on the composition of the particles over an extended range of elements and chemical compounds, including organics.

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