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## New approach using femtoseconde laser ablation coupled to ICPS for direct determination of trace elements and lead isotope ratios in crude oils and its fractions

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The development of studies dedicated to metal determination in crude oil and its fractions has increased during the last decade (mainly V, Ni and more recently Cu, Mo, Ag, Sn, Ba and Pb). Proportionality of trace metals has usually used as geochemical tracers of oil-oil, oil-source rock correlation, for identification of source rocks and quantification of oils thermal maturity and biodegradation levels. The low tolerance of the plasma toward organic solvents creates some complications (cone carbon deposit and carbon-oxygen-based interferences) for the introduction of organic matrix in the ICPMS via conventional liquid nebulisation. Dreyfus et al. (2005) show that direct introduction of dilute crude oil in the plasma by a PFA-100 MicroFlow Nebulizer associated with a Scott "double pass" chilled spray chamber gives detection limit in the  $pg.g^{-1}$ . Nevertheless, this introduction requires high dilutions of crude oil which is a limiting factor for ultra traces determination.

We have developed a new approach using a femtosecond laser for direct ultra trace element analysis in crude oils. This unique laser has the advantage to combine ultra short pulses with high repetition rate (10000 Hz), low energy and ultra-fast scanning beam device. Carbon deposit is very low thick to the low mass of sample introduced

into the plasma (tens of nL/min), and the analytical performances are drastically enhanced compared to ns laser in terms of elemental fractionation, thermal effect, sensitivity and management of sample heterogeneity. In order to optimize the ablation protocol, we have tested different oils supports, and this unique laser has permitted to test several ablation programs and different parameters (ablation velocity, surface of focalisation...).

Results have permitted to the direct measurement of trace element concentrations and lead isotope ratios in crude oil and its fractions. LA-ICP-MS lead isotope ratios determination has been validated by independent methodology using microwave-assisted digestion. Uranium and Thorium are also measured in order to date crude oil for future investigation. The first results are presented here.

Dreyfus et al. Direct trace and ultra-trace metals determination in crude oil and fractions by inductively coupled plasma mass spectrometry. *Journal of ASTM International*, 2005. Vol.2, No.9.