

Determination of Trace Elements in Geological Samples by the Combination of Flow Injection-liquid-liquid Extraction and Inductively Coupled Plasma Atomic Emission Spectrometry

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Inductively coupled plasma atomic emission spectrometry (ICP-AES) is one of the preferred methods for the simultaneous determination of multi-elements, and has been widely applied to the determination of trace elements in various materials. However, its use in trace analysis of complex samples for elements at trace or ultratrace levels is still limited owing to the insufficient sensitivity and the interference effects of matrix elements. Therefore, methods with ICP detection associated with separation and pre-concentration procedures are desirable.

Solvent extraction combined with ICP-AES is an effective approach to improving the limits of detection, meanwhile, the nebulization of the organic solvents may improve the nebulized and transported efficiencies. However, the organic solvent may cause spectral and non-spectral interference and degrade analytical performance by introducing noise. Boorn et al. pointed out that some imported organic solvents may cause the destabilization or extinction of the low-power argon ICP discharge due to the high solvent plasma loading, so the selection of organic solvents is very important. Meanwhile, the manual liquid-liquid extraction procedures are usually very tedious, the consumption of solvents is high and the volatility of organic solvents causes the environmental pollution. A very effective way to overcome the above-mentioned drawbacks is the on-line flow injection liquid-liquid extraction (FI-LLE) techniques.

In this study, the detailed information concerning the influence of organic solvents on the characteristics of ICP has been investigated with the aid of flow injection. The plasma solvent loading can be effectively controlled by adjusting the rotation speed of the flow injector's pump. The plasma excitation temperature with tributyl phosphate (TBP) loading has been detected by using Mg 278.3nm/Mg 333.67nm line intensity ratio, a high kinetic temperature exhibits by the plasma, usually above 5000K. And the plasma local thermodynamic equilibrium has been diagnosed also by using Mg 279.55nm/Mg

285.21nm line intensity ratio, value of the ratio close to the theoretical value is obtained with the use of a high power (>1.4KW), a low carrier gas flow-rate (1Lmin⁻¹) and a low solvent loading. So the plasma discharge has enough energy for atomization of the sample and excitation and ionization of the free atoms. Meanwhile, the spectrogram of organic solvents (CHCl₃, CCl₄, MIBK and TBP) has been investigated. The investigation proves that the solvent pyrolysis products (principally C, C₂ and CN) generate serious background spectral emission. However, the effect of background emission can be decreased by means of selecting optimum operating parameters of ICP and sensitive emission line of the detected elements.

A special phase separator (Lin et al., 1996) and solvent extract system of flow injection are designed for determining molybdenum and tungsten in geological samples. The studies based on NH₄SCN-TBP-Mo (W) systems indicate that the detection limits (3 ppb) are 3.6 µg/L for molybdenum and 28 µg/L for tungsten. The precision (RSD, n=7) for molybdenum and tungsten are 4.0% and 2.7% respectively. The consumption of TBP is 200 µl and the sample throughput is 25~30/h.

The same approach of FI-LLE-ICPAES is used for determining lead in environmental sample, and compared with aqueous solution. The studies based on DDTC-CCl₄-Pb extraction system and aqueous solution indicate that the detection limits are 0.14 g/ml and 6.67 g/ml, and the precision (RSD) are 4.0% and 4.2% respectively.

Boorn AW & Browmer RF, *Inductively Coupled Plasma Emission Spectroscopy*, Part Wiley, New York, Chapter 8., (1997).

Lin SL, Shuai Q & Qiu HO, *Spectrochim Acta*, Part B, 51, 1796-1798, (1996).