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On-line emulsion formation and multi-element analysis of edible oils by inductively coupled plasma atomic emission spectrometry

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Abstract

A novel simple on-line emulsion formation system for multi-element analysis by inductively coupled plasma atomic emission spectrometry (ICP-AES) was developed. A laboratory made magnetic-stirring micro-chamber was used for continuous edible emulsification with Triton X-100 and for subsequent introduction of the emulsion into ICP-AES. The optimum concentration of oil in emulsion for maximum sensitivity was 50% (v/v). The performance of the system was demonstrated for Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, Mg, Mn, Ni, Pb, Tl and Zn determination in olive, sunflower and corn oil. Good agreement was found between calibration curves for oil emulsion and aqueous ones for the most of the investigated spectral lines. The calibration curves for each element were linear at least up to 1.0 mg l^{-1} and the correlation coefficients were ranged between 0.991 and 0.999. The proposed method was applied to the analysis of olive oil sample and compared with ETAAS-wet digestion method. No significant differences were observed between the two methods.

Keywords: Inductively coupled plasma atomic emission spectrometry; On-line; Emulsion; Edible oil; Multi-element analysis

1. Introduction

The quality of edible oils with regard to freshness, storability and toxicity can be evaluated by the determination of metals. Trace levels of metals like Fe, Cu, Ca, Mg, Co, Ni and Mn are known to increase the rate of oil oxidation while other elements such as Cr, Cd, and Pb are very important on account of their toxicity and metabolic role. Thus, the development of rapid and accurate analytical methods for trace elements determination in edible oil has been a challenge in quality control and food analysis.

Various techniques like electrothermal atomic absorption spectrometry (ETAAS) [1], inductively coupled plasma atomic emission spectrometry (ICP-AES) [2] or mass spectrometry (ICPMS) [3,4] and voltammetry [5] have been employed for analysis of edible oils. However, sample pretreatment procedures like: wet or dry digestion, microwave digestion, dilution with organic solvent and some extraction methods are required, in order to eliminate the organic matrix. These techniques are usually difficult to be automated, time consuming, laborious and prone to contamination and losses. On the other hand, direct analysis of samples with high content of organic matrix by ICP techniques encounters many drawbacks and usually causes plasma to be extinguished. Another negative effect is the injector blocking due to carbon deposition from incomplete oxidation of organic matrix [6]. An alternative technique for introduction of oil samples directly into inductively coupled plasma (ICP) is the on-line emulsification [2,7], which also offers some other advantages like using aqueous standards solutions for calibration and quantification, reduction of matrix interference, higher sampling frequency and lower cost of analysis. Direct introduction of oil samples in the form of emulsion into ICP considerable simplifies the spray chamber and plasma torch because no extra oxygen or complicated desolvation device is needed. In this case, the use of stable emulsions with proper surfactant concentration is very important. The on-line prepa-

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ration of emulsions in FI systems, which have been reported in literature [3,8,9] make use ultra-sonic bath with serious drawbacks in efficient preparation of stable emulsions.

In this work, a magnetic-stirring micro-chamber was developed and elaborated for on-line emulsification and direct introduction into ICP oil-in-water (o/w) emulsions with high oil concentration. To our best knowledge stirring chamber for on-line emulsification has not been reported in flow injection (FI) systems. The proposed manifold was optimized for on-line multi-element determination of Ag, Al, B, Ba, Bi, Ca, Cd, Co, Cr, Cu, Fe, Ga, In, Mg, Mn, Ni, Pb, Tl and Zn in edible oil using Triton X-100 as emulsifier. Finally, the use of aqueous standard solutions for calibration and quantification of edible oil samples has been tested and it was proved that can be successfully applied.

2. Experimental

2.1. Instrumentation

All experiments were carried out using a Perkin-Elmer Optima 3100 XL axial viewing ICP-AES, according to the operating conditions given in Table 1. The investigated elements and their spectral lines, which have been studied, are also presented in Table 1. A Perkin-Elmer model 5100 PC atomic absorption spectrometer equipped by Zeemann effect background correction and a transversely heated graphite tube atomizer (THGA), was employed for Al, Ca, Cr, Cu, Fe, Mg and Mn determination, using the instrument conditions given in Table 2. The manifold for on-line emulsion formation of edible oil samples and for the subsequent introduction of emulsions in the ICP-AES is presented in Fig. 1. It consists of two peristaltic pumps (P1 and P2, Gilson minipuls 3), a six-port two-position injection valve (IV, Labpro, Reodyne, USA) and a laboratory made magnetic-stirring micro-chamber (SC), which was manufactured and employed for on-line emulsification.

Table 1
Operating conditions and description of the ICP-AES instrument

RF generator (MHz)	40 (free-running)
RF incident power[a] (W)	1500
Argon flow rates ($\mathrm{l\,min^{-1}}$)	0.5 (auxiliary); 15 (plasma)
Nebulizer gas flow rate[a] ($\mathrm{l\,min^{-1}}$)	0.7
Spray chamber	Scott double-pass
Nebulizer type	Gem tip cross flow
Nebulizer uptake flow rate[a] ($\mathrm{ml\,min^{-1}}$)	2.0
Detector	Segmented-array charge-coupled (SCD) 235 sub-arrays
Studied elements and their spectral lines	
Ag (nm)	328.068/338.289
Al (nm)	237.313/308.215
B (nm)	249.772/208.957
Ba (nm)	233.527
Bi (nm)	223.061/190.171
Ca (nm)	317.933/396.847
Cd (nm)	228.802/214.440
Co (nm)	238.892/228.616
Cr (nm)	284.325/283.563
Cu (nm)	224.700/327.393
Fe (nm)	259.939/238.204
Ga (nm)	294.364
In (nm)	325.609/230.606
Mg (nm)	279.077/280.271
Mn (nm)	257.610/259.372
Ni (nm)	221.648/232.003
Pb (nm)	220.353/217.000
Tl (nm)	276.787/190.801
Zn (nm)	213.857/202.548

[a] Optimised value.

Table 2
Operation conditions of ETAAS instrument

	Al	Ca	Cr	Cu	Fe	Mg	Mn
Wave length (nm)	309.3	422.7	357.9	324.8	248.3	285.2	279.5
Pyrolysis temperature (°C)	1200	1100	1300	800	1000	800	600
Atomization temperature (°C)	2300	2500	2500	2500	2500	1900	2500
Reading time (s)	4	4	5	5	5	4	5

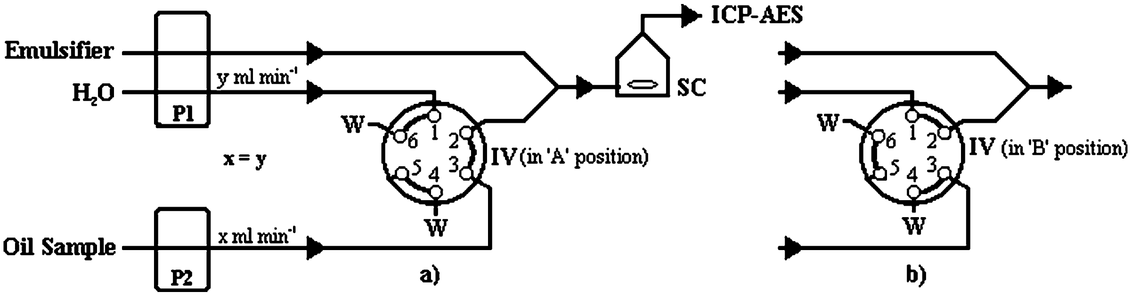

Fig. 1. Schematic diagram of continuous flow manifold, for on-line emulsification and ICP-AES determination. P1 and P2, peristaltic pumps; IV, injection valve; SC, magnetic-stirring micro-chamber; emulsifier, Triton X-100 2% (v/v) aqueous solution; W, waste. (a) Sample measurement mode IV is in "A" position and (b) calibration mode IV is in "B" position.