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Determination of fluorine in Turkish wines by molecular absorbance of CaF using a high resolution continuum source atomic absorption spectrometer

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ABSTRACT

Fluorine contents of different types of wines produced in Turkey were determined by the molecular absorption of calcium mono-fluoride (CaF) using a high resolution continuum source graphite furnace atomic absorption spectrometer (HR-CS GFAAS). For this purpose, 2000 μg mL^{-1} of calcium was co-injected to the graphite furnace with diluted wine samples. In order to increase the sensitivities and reduce the limit of detection (LOD) and characteristic mass, summation of the absorbances for CaF at 606.440 nm and 606.231 nm were evaluated. Graphite furnace program was optimized for best accuracy and 700 °C for pyrolysis, 2250 °C for molecule forming temperature was selected. Quantification was made by linear calibration, standard addition technique by HR-CS-AAS and the results were also compared with ISE method and no significant difference was found. The range of F contents for 20 red and white wine samples varies between LOD and 0.38 mg L^{-1}. The limit of detection and characteristic mass of the method were 0.18 and 0.058 ng of F, respectively which are appropriate to detect the fluorine concentrations in most of the wine samples. The method is simple, fast, accurate and sensitive.

1. Introduction

Fluorine which is an inevitable part of human life, is found abundantly in nature. Since 1945, fluoride has been added to water supplies around the world starting in the USA in order to prevent dental decay (Ripa, 1993). Daily allowance of fluoride ion from all sources is set at 0.05 mg/kg body weight for all ages above 6 months (Ponikvar, 2008). This amount of fluorine intake is needed for preventing dental caries, however chronic exposure to fluorine can interfere with bone formation and can cause death by blocking various enzymes (Chachra, Limeback, Willett, & Grynpas, 2010). In daily life, fluoride exposure can be caused by various sources like processed foods made with fluoridated water, fluoride containing pesticides, bottled teas, fluorinated pharmaceuticals, etc. (The Fluoride Action Network, 2014). According to the U.S. Environmental Protection Agency (EPA) (2010), fluoride is present in a number of alcoholic beverages, especially wines, due to the use of cryolite as a pesticide on grapes. In addition, fluoride in wine can be caused by irrigation waters (Martinez, Diaz, Borges, Diaz, & Perez, 1998). The maximum limit of F concentration in wines recommended by International Office of the Wineyard and the Wine (1990) is 1 mg L^{-1}. Burgstahler and Robinson (1997) found the fluoride levels of 19 California wines as 0.23–2.80 μg mL^{-1}, Martinez et al. (1998) reported the mean fluoride concentrations in 70 wines from the Canary Islands ranging from 0.08 to 0.68 μg mL^{-1} and USDA (2005) reported 1.05 μg mL^{-1} of fluoride in 14 red wine samples and 2.02 μg mL^{-1} of fluoride in 17 white wine samples.

For years, atomic absorption spectroscopy (AAS) has been a routine method for determination of trace metals and metalloids (Welz, 2005). Fluorine cannot be directly determined by conventional line source atomic absorption spectrometer (LS AAS) since its atomic absorption wavelength is in vacuum UV (95 nm) where air components absorb as well (Ozbek & Akman, 2013). However, after recent developments in high-resolution continuum source atomic absorption spectrometry (HR-CS AAS), fluorine and other halogens can be easily determined. The method is based on the formation of a diatomic molecule in the gas phase of the flame or graphite furnace of AAS between F and an externally added appropriate metal to the samples/standards and the measurement of the molecular absorption of formed diatomic molecule's well-defined fine

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structured rotational lines. However, this method is not successful with conventional AAS because any emission line of a hollow cathode lamp (HCL) generally does not exactly overlap with the very narrow rotational line of the diatomic molecule. In addition, the method suffers from spectral interferences due to the overlapping of the isolated emission band with neighboring absorption lines for some gaseous species originated from the sample matrix. However, HR-CS AAS with a high intensity xenon short arc lamp, high resolution double monochromator (a prism for pre-dispersion and an Echelle grating for high resolution) and a charged couple device (CCD) detector, it is possible to obtain the ultra-fine emission and measure the molecular absorption at exactly the rotational line of the diatomic molecule with adjusted line-width. In addition, the time and wavelength spectra in the vicinity of the working wavelength can be visualized. There are some studies for determination of fluorine by HR-CS AAS using molecular absorption of AlF (Ozbek & Akman, 2012a) and GaF (Gleisner, Einax, Mores, Welz, & Carasek, 2011; Gleisner, Welz, & Einax, 2010; Kruger et al., 2012), CaF (Mores, Monteiro, Santos, Carasek, & Welz, 2011; Ozbek & Akman, 2013) and SrF (Ozbek & Akman, 2012b). Welz et al.(2009) and Butcher (2013) reviewed the fluorine determinations performed by LS AAS and HR-CS AAS, thoroughly. Eventually, atomic absorption spectrometer, which is basically used for metal and metalloid determination, could be successfully benefited for fluorine determination. The total fluorine (ionic and covalently bond) is determined via molecular absorption of diatomic molecules using HR-CS AAS whereas ion chromatography (IC) and ion-selective electrodes (ISE) are suitable only for the determination of ionic fluoride. In addition, both techniques (IC + ISE) require the control of ionic strength (Gleisner et al., 2011). Inductively coupled plasma atomic emission spectrometry (ICP-AES) is not suitable for fluorine determination because the atomic and ionic emission lines are in vacuum UV range. Inductively coupled plasma mass spectrometry (ICP-MS) is not suitable as well due to high ionization potential of fluorine. The drawbacks of ISE, IC and some other methods which have been used for fluorine/fluoride analysis were discussed extensively in many papers.

In this study, total fluorine (ionic and covalently bond) in Turkish wine samples were determined by high-resolution continuum source molecular absorption spectrometry (HR-CS MAS). Calcium was used as a molecule forming element and the molecular absorption of calcium monofluoride (CaF) at 606.440 nm and 606.231 nm were summated to improve the LOD and characteristic mass values. The experimental and instrumental parameters were optimized.

2. Experimental

2.1. Instrumental

All measurements were done in graphite furnace of an Analytik Jena ContrAA 700 high resolution continuum source atomic absorption spectrometer equipped with a 300 W xenon short arc lamp (XBO 301, GLE, Berlin, Germany), high resolution double monochromator, consisting of a prism for pre-dispersion, an echelle monochromator and a charge-coupled device (CCD) array detector. The resolution ranged from 1.6 pm per pixel at 200 nm, to 6.4 pm at 800 nm. All measurements were made using pyrolytically coated graphite tubes with integrated PIN platform (Analytik Jena Part No. 407-A81.025) at 606.440 nm and 606.231 nm simultaneously with 3 + 3 pixels (central pixels ± 1). All solutions were pipetted as 10 μL. As blank solution, 10 μL of 2000 μg mL^{-1} (i.e. 20 μg) of Ca in 10% ethanol solution is used.

Fluoride in wine samples was also measured using a fluoride-selective electrode (Orion 9609BNWP with Orion pH/ISE meter 710, both Thermo Scientific, Waltham, MA, USA). Total ionic strength adjustment buffers (TISAB) (TISAB II, Orion Research Inc., Beverly, Mass, USA) were added to all wine samples at a ratio of 1:1. Calibration was performed with standard solutions prepared from NaF using Tris buffer to account for ionic strength.

All glassware and polyethylene flasks used for solutions preparations were previously immersed in a 10% (v/v) HNO_3 bath overnight and then rinsed with ultra-pure water to avoid contamination.

2.2. Reagents and solutions

In all dilutions, high purity water with 18.2 MΩ cm resistivity obtained from a TKA reverse osmosis and a TKA deionizer system (TKA Wasseraufbereitungsysteme GmbH, Niederelbert Germany) was used. 10,000 μg mL^{-1} of fluorine and calcium stock solutions were prepared from NaF and $Ca(NO_3)_2 \cdot 4H_2O$ and diluted daily. Inorganic acids and reagents were of analytical grade (HNO_3, 65% (v/v), $Ca(NO_3)_2 \cdot 4H_2O$, NaF; Merck, Darmstad, Germany). The waste water standard reference material SPS-NUTR-WW2 (which includes 10.0 ± 0.1 μg mL^{-1} of F^-, 50.0 ± 0.5 μg mL^{-1} of Cl^-, 7.5 ± 0.08 μg mL^- of PO_4^{3-}, 5.0 ± 0.05 μg mL^{-1} of $NO_3^-$and 100 ± 1 μg mL^{-1} of SO_4^{2-}) was provided byLGC Standards (Middlesex, England). White wine and red wine samples of different brands and origins were purchased from markets in Istanbul, Turkey.

2.3. Procedure

Samples and 2000 μg mL^{-1} of calcium prepared from $Ca(NO_3)_2 \cdot 4H_2O$ were co-injected into the graphite tube as 10 μL from each. Fluorine determination was performed by HR-CS GFAAS via evaluating the rotational molecular absorption lines of CaF at 606.440 nm and 606.231 nm simultaneously. The optimized graphite furnace program is given in Table 1. Certified reference standard was diluted 10 times before analyses. Analyses were performed both by linear calibration and standard addition. All results were given as the mean of at least three replicates.

3. Results and discussion

3.1. Selection of wavelength

The method is based in the molecular absorption measurement of CaF generated in the gas phase of a graphite furnace. It was stated that the diatomic species with bond dissociation energies higher than 500 kJ mol^{-1} are suitable to use for the determination of non-metals. Since the dissociation energy of CaF is 529 kJ mol^{-1}, it is suitable for this purpose (Mores et al., 2011). In the literature, 606.440 nm is a part of the rotational fine structure of the $X^2\Sigma^+ - A^2\Pi$ electronic transition and was found to be the most appropriate working wavelength due to highest sensitivity of all

Table 1
The optimized graphite furnace temperature-time program for the determination of fluorine via MAS of CaF.

Step	Temperature (°C)	Ramp (°C s^{-1})	Hold time (s)	Gas flow, (L min^{-1})
Drying	80	6	20	2.0
Drying	90	3	20	2.0
Drying	120	5	10	2.0
Pyrolysis	700	300	10	2.0
Gas adaption	700	0	5	Stop
Molecule formation	2250	2000	5	Stop
Cleaning	2500	500	4	2.0