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Investigation of interference mechanisms of nickel chloride on copper determination and of colloidal palladium as modifier in electrothermal atomic absorption spectrometry using a dual cavity platform

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Abstract

The interference of nickel chloride on the determination of copper by electrothermal atomic absorption spectrometry was investigated using a specially designed dual cavity platform (DCP), which allows the analyte and interferent to vaporize from separate cavities, so that gas and condensed phase interferences can be distinguished to some extent. It was found that, when low pyrolysis temperatures were used, the interference of nickel chloride on copper originated from the formation of copper chloride in the condensed phase, which is not efficiently dissociated in the atomization stage. Alternately, when analyte and interferent were in separate cavities of the DCP, a gas-phase reaction between copper and chlorine in the atomization stage resulted in a similar signal depression. When higher pyrolysis temperatures were used, interference could be attributed to losses of volatile copper chloride in the pyrolysis stage. These losses were more pronounced when analyte and interferent were in separate cavities of the DCP, indicating again a gas-phase reaction between copper and chlorine, as well as a protective action of nickel oxide, when analyte and interferent were mixed. Colloidal palladium used as modifier removed the chloride interference independent of the pyrolysis temperature applied, when copper and nickel chloride were mixed. Colloidal palladium also increased the integrated absorbance for copper by 40–50%, even when analyte and modifier were in separate cavities of the DCP, indicating a strong gas-phase interaction between copper atoms and the modifier through adsorption/desorption processes.

Keywords: Copper; Electrothermal atomic absorption spectrometry; Nickel chloride interference; Colloidal palladium modifier; Dual cavity platform

1. Introduction

The interference mechanism of chloride-containing salts on the atomization of various analytes in electrothermal atomic absorption spectrometry (ET AAS) has been investigated in numerous papers. The mechanisms proposed can be summarized as follows: (i) gas-phase combination reaction between analyte and matrix decomposition products in the atomization stage [1,2]; (ii) occlusion of the analyte in matrix micro particles, which are carried out of the tube without decomposing in the atomization stage [3–5]; (iii) expulsion of analyte atoms together with rapidly expanding matrix gases in the atomization stage [5–8]; (iv) formation of a thermally stable compound of analyte with matrix constituents, which is not as efficiently atomized as matrix-free analyte [1,6,9,10]; (v) formation of a volatile compound between analyte and matrix in the condensed phase and its vaporization in molecular form in the pyrolysis stage [6–9,11]. However, most of the interferences reported in early publications have been overcome by using an appropriate modifier under Stabilized Temperature Platform Furnace (STPF) conditions [12]. In spite of all efforts and advances in ET AAS technique, some interference could not be completely avoided or eliminated. It is important, therefore, to understand the origin of interferences in order to provide proper conditions for interference-free determination.

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Table 1
Temperature program used for the determination of copper

Stage	Temperature (°C)	Time (s)		Internal gas flow rate (ml min^{-1})
		Ramp	Hold	
Drying 1	110	10	15	300
Drying 2	150	5	15	300
Pyrolysis	Variable	10	20	300
Atomization[a]	2200	0	5	0
Clean	2650	1	5	300
Cool	20	2	6	300

[a] Read in this stage.

The aim of this work is to investigate the interference of nickel chloride on the determination of copper by ET AAS under STPF conditions by using a dual cavity platform (DCP), which has been used successfully in earlier work of ours [6,8,13] to investigate interference mechanisms. The DCP, in principle, makes possible separating interferences occurring in the gas phase from those in the condensed phase, and it reveals gas/condensed phase interaction. In addition, the interaction of analyte with palladium modifier in the DCP with and without nickel chloride was investigated.

2. Experimental

2.1. Instrumentation

A Perkin-Elmer Z/3030 atomic absorption spectrometer with Zeeman-effect background correction, equipped with an HGA-600 graphite furnace was used in this work. A copper hollow cathode lamp was used as the spectral radiation source at 324.8 nm. Custom-made dual cavity platforms (Ringsdorff Werke GmbH, Bonn, Germany, RW0553/4) of total pyrolytic graphite were used throughout this work. They were inserted into Perkin-Elmer pyrolytic graphite coated tubes (Ringsdorff, Bonn, Germany, RW0555/9-HD-Pyc) in which the dosing hole was enlarged to form a slot in order to facilitate injection into the two separate cavities of the DCP. All solutions were injected manually with a 10-μl Eppendorf pipette. Nitrogen was used as the purge gas. The operating parameters for the graphite furnace for Cu are presented in Table 1.

2.2. Reagents

Stock solutions containing 1000 mg l^{-1} Cu were prepared from $Cu(NO_3)_2$ (Merck). Stock matrix solution was prepared from analytical reagent grade $NiCl_2$. Colloidal palladium was prepared from palladium chloride by addition of polyvinylpyrrolidone (PVP) as described elsewhere [14]. All test solutions were diluted to appropriate concentrations with distilled–deionized water before use.

3. Results and discussion

3.1. Influence of nickel chloride on copper

The influence of nickel chloride on the integrated absorbance signal of copper under different experimental conditions is shown in Fig. 1. Copper in pure aqueous solution is thermally stable up to a pyrolysis temperature of about 1200 °C, and is rapidly volatilized at higher temperatures. In the presence of nickel chloride, and when pyrolysis temperatures of 400 °C or less were used, a 60% lower integrated absorbance is obtained, irrespective of whether copper is mixed with nickel chloride or deposited in separate cavities of the DCP. A dramatic change with a 100% analyte recovery was observed when copper was mixed with nickel chloride, and a pyrolysis temperature of 600 °C was used. This effect, however, was only obtained for this temperature, whereas increasing losses of copper were found for higher pyrolysis temperatures. In contrast, when analyte and interferent were in separate cavities of the DCP, the increase in recovery at 600 °C was marginal, and essentially disappeared for higher pyrolysis temperatures. At 1200 °C, the two curves joined and dropped further in the same way.

In a second set of experiments, first nickel chloride in aqueous solution was pipetted onto the platform, dried and thermally pretreated at different pyrolysis temperatures. Then the program was interrupted, and after the tube had cooled, the copper solution was injected on top of the thermally pretreated nickel chloride, dried, pyrolized at the same temperature used previously for nickel chloride, and atomized. The results are shown in Table 2. When nickel chloride was thermally pretreated at 200 or 400 °C, the integrated absorbance for copper was essentially the same as when the solutions were mixed (see Fig 1). However, when nickel chloride was thermally pretreated at 600, 800, 1000 or 1200 °C before copper was added, the same integrated

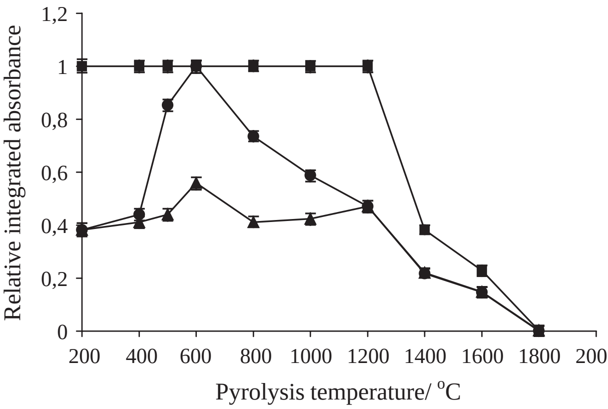

Fig. 1. Pyrolysis curves for 1 ng Cu as the nitrate in the presence of 10 μg of nickel as the chloride in aqueous solution in the DCP; (■) copper alone; (●) copper mixed with nickel chloride; (▲) copper and nickel chloride in separate cavities. Average and standard deviation of $n=3$ measurements each.