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X-Ray Fluorescence Determination of Trace Elements in Vitamin-Mineral Complexes and Medicinal Herbs Using Chemically Modified Polyurethane Foam Sorbents

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Abstract

In this paper, we proposed the method of X-ray fluorescence (XRF) for the determination of some essential trace elements in medicinal herbs and vitamin-mineral complexes at the level of 1-10 μg/ml. To increase sensitivity and selectivity of the determination, we followed simple and effective approach based on the extraction of metal ions from aqueous solutions with chemically modified polyurethane foam sorbents followed by direct XRF analysis. The conditions of sorption preconcentration of Co (II), Ni (II) and Zn(II) ions with modified sorbents were optimized. The proposed approach is used for the determination of trace elements in several kinds of medicinal herbs (coltsfoot leaves, nettle leaves and yarrow herb) and vitamin-mineral complexes (Alfavit, Vitrum and Multi-tabs).

Keywords: Trace elements, Medicinal herbs, Vitamin-mineral complexes, Polyurethane foam sorbent, X-ray fluorescence analysis.

Introduction

Trace elements are essential parts of most important enzymes. Insufficient or excess intake of trace elements leads to disruption of metabolic processes and to various diseases consequently (1). Vitamin-mineral complexes are traditionally used for the prevention and treatment of the lack of trace elements. Moreover, medicinal herbs also can be the source of trace elements. Thus, determination of trace elements in plant samples and in mineral complexes is one of the priority tasks of pharmaceutical analysis.

The content of various trace elements in vitamin-mineral complexes varies from μg to mg per gram of drug. Along with trace elements a significant amount of both active and auxiliary organic substances contained in the above mentioned drugs. The content of the vital elements per gram in medicinal herbs is about tens of nanograms (2). Concentration of the inorganic components in plants is a few percents of mass. Because of the complexity of drug and plant matrices, it is necessary to use only high selective and high sensitive methods (inductively coupled plasma atomic emission spectroscopy (ICP-AES), for example) for determination of trace elements in these objects (3). Limits of traditionally used techniques of trace metals analysis are slow rapidity, high energy consumption during thermal mineralization, high cost of analysis, singleton determination (4).

The purpose of this research is the development of alternative way of determination of vital trace elements in medicinal herbs and vitamin-mineral complexes without limits of traditional approach. The following tasks are necessary for achieving this purpose:

-to choose the most available and effective chemical-instrumental approach to increase selectivity and sensitivity of determination of trace elements;

-to minimize the number of stages of developed techniques for increasing accuracy and rapidity of determination of trace elements ; to optimize the conditions of sample preparation for individual and group determination of these trace elements ; to choose measuring tool and optimal conditions of formation of the analytical signal.

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Materials and Methods

Reagents and materials

Ether-based polyurethane foam (PUF) (Radical, Kiev, Ukraine) is used for the concentration of trace elements from medicinal herbs and vitamin-mineral complexes. The size of PUF tablets for sample preparation is 10 × 10 × 1 mm. The geometric shape of these tablets is parallelepiped. The degree of purification was monitored by XRF method. In our work state standard samples containing 1 mg/mL Ni(II), Zn(II), Co(II) ions (Ecoanalytica, Moscow), resorcinol (pure for analysis), 8-hydroxyquinoline (pure for analysis), 2-nitroso-1-naphthol (pure for analysis), sodium nitrite (chemically pure), sodium hydroxide, hydrochloric acid, acetic acid (high purity) «Sigma-Aldrich, USA), coltsfoot leaves, nettle leaves, yarrow herb (all-Krasnogorskleksredstva LLC, Russia) and vitamin-mineral complexes «Alfavit» (Recordati Group, India), Vitrum (Unipharm, Inc., USA), Multi-tabs (Ferrosan, Denmark) are used.

Preparation of chemically modified sorbent

The mass of PUF sorbent is 25 mg. The prepared PUF tablets were washed with 1 M HCl during 1 hour and then with distillated water up to pH 5-6, because PUF may contain a technological metal impurity, especially, zinc. The technique of chemical modification of PUF sorbent is based on diazotization and subsequent azo-coupling reaction with an organic reagent. This reaction takes place with toluidine end groups of macromolecules of PUF sorbent. The scheme of chemical modification of PUF sorbent is shown in Fig. 1 (5). Molecules of the reaction product have functional and analytical chelating groups. 8-hydroxyquinoline is used for extraction Ni(II), Zn(II) ions (6), resorcinol - for extraction Co(II), Ni(II) ions (7) and 2-nitroso-1-naphthol - for extraction Co(II) ions respectively (8).

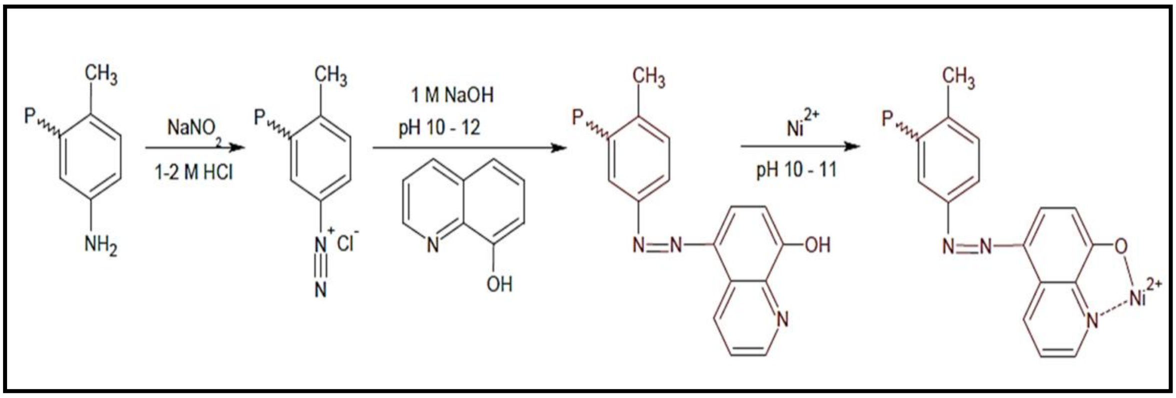

Figure 1. The scheme of chemical modification of PUF sorbent

PUF diazotization was carried out as follows. 30 mL 1 M HCl and 200 μg PUF sorbent were placed in a glass vessel for extraction lapped cover. PUF tablet pressed with a glass rod to remove air bubbles. After the addition of 15 mg $NaNO_2$ the content of extraction vessel was shaken on a mechanical vibromixer for 30 minutes (5). After that tablet of diazotized PUF sorbent was removed from the solution and dried between sheets of filter paper. Then it was used in azo-coupling reaction. 20 mg of resorcinol (or 20 mg of 8-hydroxyquinoline, or 15 mg 2-nitroso-1-naphthol) was dissolved in 30 mL NaOH (pH 10) in another vessel for extraction. The diazotized PUF tablet was added to this solution, air bubbles was removed. The obtained solution was stirred for 60 minutes. After that, PUF tablet was washed and dried, as it described before. Tablets of a size 10 × 10 × 1 mm were cut from the chemically modified sorbent. The purity of the PUF sorbent was monitored by XRF method.

Concentration of trace elements.

For the preparation of samples to 25 mL of an aqueous solution containing from 0.1 to 50 µg/mL Ni(II), Zn(II), Co(II) ions is added one tablet PUF sorbent modified by 8-hydroxyquinoline, resorcinol and 2-nitroso-1-naphthol. The air was removed from PUF tablets. Contents of extraction vessels were shaken for 80 minutes. After that PUF tablet was removed from the solution, it was thoroughly washed with distilled water and was dried between sheets of filter paper.

Sample preparation of medicinal herbs and vitamin-mineral complexes (9).

Weights of the analyzed medicinal herbs (m = 5-10 g) and vitamin-mineral complexes (m = 2-2.5 g) were thoroughly ground in an agate mortar to a homogeneous powder. Weights of this powder were placed in polytetrafluoroethylene glass, 8 mL 70 % HNO_3 and 2 ml 30 % H_2O_2 solutions were added. The obtained solution was heated on hotplate at the temperature 100-110 °C until no brown fumes NO_2 was observed. After mineralization obtained mixture was filtered on glass filter crucible. The filtrate was quantitatively placed into the extraction vessel. The volume of solution was adjusted to 25 mL using of 0.1 M NaOH. The tablets of chemically modified PUF sorbent were placed into this solution. The air was removed from PUF tablets. Contents of extraction vessels were shaken for 80 minutes. After that PUF tablet was removed from the solution, it was thoroughly washed with distilled water and was dried between sheets of filter paper.

Measurement of analytical signal.

Direct XRF determination of trace elements on chemically modified PUF sorbent was performed on a Spectroscan G Max XRF spectrometer (LLC Spectron, St. Petersburg, Russia). The instrument was equipped with gas-filled proportional counter tube (filler gas 90% Xe + 10% CH_4 under atmospheric pressure, the thickness of the Be window is 150 μm), LiF(200) crystal analyzer ($2d$ = 402.8 pm), and low-power (4 W) sharp-focus (∅ 1.5 mm) X-ray tube of the transmitted type with a thin-film (2 μm) Mo-anode (the thickness of the Be window is 200 μm). The working voltage was 40 kV. The current was 100 μA. The incidence angle of the primary radiation on the sample surface was 80°, and the takeoff angle of the secondary radiation was 30°.

To determine XRF spectra, PUF tablets were placed in specially made cuvette with low level of scattered primary radiation (10-12). The peak value of the line intensities $\mathrm{Co}K_\alpha$, $\mathrm{Ni}K_\alpha$, $\mathrm{Zn}K_\alpha$ in wavelength ranges 179.0 ± 5; 165.9 ± 5; 143.5 ± 5 pm respectively were measured for each sample. The exposure time is 60 s. The analytical signal is integrated intensities of the lines of these elements excluding the background signal normalized to the intensity of the scattered radiation $\mathrm{Mo}K_\alpha$ is incoherent X-ray tube.

Results and Discussion

Selection conditions of modification of PUF sorbent.

The end toluidine groups of PUF in hydrochloric acid react with aqueous solutions of alkali metal nitrites with the formation of yellow solution of diazonium cation. Diffuse reflectance spectroscopy shown that maximum yield of diazotized PUF is achieved after 30 minutes of phase contact in 1-2 M HCl (12).

It was known that diazotization of monomeric aromatic amines usually occurs at lower temperatures (0-7 °C). It complicates the modification of PUF sorbent. In the paper (13) was shown that diazotization of PUF is possible at room temperature. Moreover, unlike the monomeric diazonium cation – very unstable compound – diazonium chloride polymer is stable in storage of diazotized PUF samples on the air for about an hour.

In the study of the chemical properties of diazotized PUF sorbent, it was shown that polymeric diazonium cation has high reactivity, similarly to monomer form. In particular, it is capable of reacting azo-coupling. The interaction of diazotized PUF with solutions of modified agents, such as 8-hydroxyquinoline, resorcinol and 2-nitroso-1-naphthol was studied. The amounts of modified reagents were taken in a 100-fold excess to the one of diazotized PUF. About azo-coupling reaction judged by color change of PUF tablets. In the presence of 8-hydroxyquinoline, resorcinol and 2-nitroso-1-naphthol PUF sorbent changes color from light yellow to orange, red and brown, respectively. Since only the active form of diazo-compounds in the azo-coupling reaction is a diazonium cation, it is necessary to maintain the pH of the solution at the level of 9.0 – 10.0.

Selection of complexation conditions.

PUF chemically modified by 8-hydroxyquinoline, resorcinol and 2-nitroso-1-naphthol is chelating sorbent for concentration of trace elements from solution, derived by mineralization of medicinal herbs and vitamin-mineral complexes. It is important to choose of optimal conditions of sorption concentration of trace elements from aqueous solutions.

It was shown that the acidity is a significant parameter for the absorption of metal ions from solution and on the selectivity of determination of Ni(II) in the presence Co(II) and Zn(II). The optimal values of pH for sorption concentration of trace elements ions are studied in our work (Fig. 2). The optimal time of sorption for Co(II), Ni(II) and Zn(II) ions is also defined. It is 60 minutes (Fig. 3). The metrological characteristics of XRF determination of trace elements using chemically modified PUF sorbents are presented in Table 1.

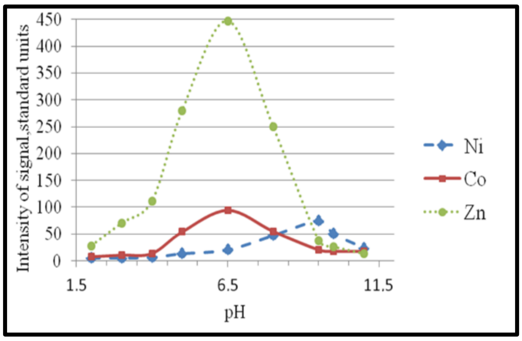

Figure 2. Selection of pH for trace metal sorption concentration (intensity of signal is average for all types of sorbent).

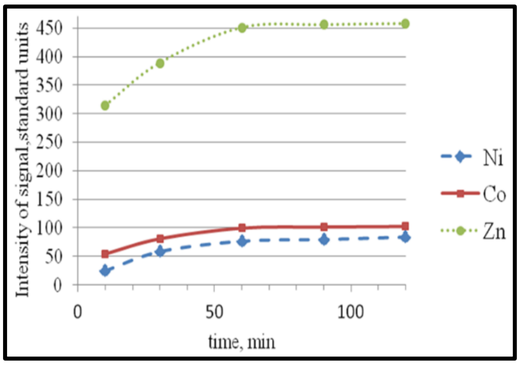

Figure 3. Selection of time for trace metal sorption concentration (intensity of signal is average for all types of sorbent).

Some other transition metals can also form the stable complexes with chemically modified PUF, but it probably can't interfere determination of zinc, cobalt and nickel in pharmaceutical objects because of excess of PUF's reaction groups and very low concentration of metals.

Proposed conditions make it possible to increase the sensitivity and linearity of range of the calibration curves by an order of magnitude as compared to existing hybrid sorption XRF techniques.

Analysis results of medicinal herbs and vitamin-mineral complexes.

The proposed approach is applied for the analysis of several kinds of medicinal herbs (coltsfoot leaves, nettle leaves and yarrow herb) and vitamin-mineral complexes (Alfavit, Vitrum and Multi-tabs). The results of Co, Ni and Zn determination in some species of medicinal herbs and vitamin-mineral complexes are presented in Tables 2 and 3. The obtained values of contents of trace elements in medicinal herbs in good agreement with the ones of AES analysis, conducted as prescribed in European Pharmacopeia 9.0 (Table 2). This fact confirms the adequacy of the proposed approach. The contents of trace elements in vitamin-mineral complexes correspond to the values declared by the manufacturer (Table 3).

Table 1. Metrological characteristics of XRF determination of trace elements using chemically modified PUF sorbents

Type of sorbent	Element	r^2	Range of quantification, µg/mL	$S_r(C_H)$
PUF, modified by resorcinol	Ni	0.985	0.5-2.5	0.04
	Zn	0.976	0.5-15	0.07
	Co	0.981	1.0-15	0.05
PUF, modified by 8-hydroxyquinoline	Ni	0.997	0.3-30	0.06
	Zn	0.996	0.2-17	0.03
	Co	0.998	0.7-17	0.08
PUF, modified by 2-nitrozo-1-naphthol	Zn	0.976	1-10	0.03
	Co	0. 985	0.7-17	0.08

Table 2. Results of trace element determination in medicinal plants (µg/g, n = 5, P = 0.95)

Metal ion	Type of sorbent*	Vitrum®		Multi-tabs® Classic		Alphavit® Classic	
		determined	specification	determined	specification	determined	specification
Zn	1	14.7 ± 1.7	15	14.2 ± 1.5	15	16.2 ± 2.7	15
	2	14.8 ± 1.5		14.1 ± 2.1		16.3 ± 1.8	
	3	14.9 ± 1.8		14.3 ± 1.9		15.8 ± 2.1	

*****1 - PUF, modified by resorcinol 2 - PUF, modified by 8-hydroxyquinoline 3 - PUF, modified by 2-nitrozo-1-naphthol

Table 3. Results of trace element determination in vitamin-mineral complexes (µg/g, n = 5, P = 0.95)

Metal ions	Type of sorbent*	Coltsfoot leaves		Nettle leaves		Yarrow herb	
		XRF	AES	XRF	AES	XRF	AES
Zn	1	98 ± 8	101 ± 11	48 ± 2	41 ± 3	45 ± 1	48 ± 8
	2	119 ± 18		47 ± 3		50 ± 4	
	3	111 ± 11		39 ± 5		38 ± 1	
Co	1	4 ± 1	4 ± 1	9 ± 1	8 ± 2	6 ± 1	6 ± 2
	2	6 ± 1		8 ± 1		6 ± 1	
	3	5 ± 1		11 ± 2		8 ± 1	
Ni	1	7 ± 1	9 ± 1	4 ± 1	4 ± 1	3 ± 1	3 ± 1
	2	10 ± 2		4 ± 1		2 ± 1	

*****1 - PUF, modified by resorcinol 2 - PUF, modified by 8-hydroxyquinoline 3 - PUF, modified by 2-nitrozo-1-naphthol

Conclusion

Developed technique of XRF determination of trace elements in medicinal herbs and vitamin-mineral complexes is simple and effective alternative to traditional used methods of atomic spectroscopy. Unlike these methods, the proposed technique does not involve using of fuel (compared with AAS) or expensive high-quality argon (compared with ICP-AES).

The sorption-XRF method is the optimal method of determination of trace elements. XRF method allows simultaneous multi-element analysis of samples, but it has not very high sensitivity of determination. The advantages of hybrid sorption-XRF approach are rapidity, low cost, sufficient sensitivity due to preliminary sorption concentration of trace elements.

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