

Suspension Columns with Grain Sorbents Retained in an Ultrasonic Field for Separation and Determination of Rare-Earth Elements in Wines

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Abstract—The properties of a Diasorb-130-IDK sorbent based on silica gel with a grain size of about 6 μm were studied in order to choose conditions for the separation of the rare-earth elements from the samples of natural wine and their subsequent determination by inductively coupled plasma mass spectrometry. The possibility of the quantitative separation of the elements with the use of an ultrasonic flow suspension column was demonstrated. The results were compared with data obtained with the use of other sample preparation methods. A procedure was proposed for the determination of the rare-earth elements and yttrium in the samples of wines.

Keywords: suspension columns, ultrasound, rare-earth metals, wine

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Sorption methods for the preconcentration of analytes are widely used in analytical chemistry. Various grainy sorbents are commonly used in the form of packed beds retained in a column or cartridge with the aid of filters from propylene, glass wool, or another porous material, which makes it possible to avoid sorbent losses upon passing the flow of a liquid test sample, washing solution, or eluent through the column [1–3]. In the majority of cases, sorbent grains with a diameter of 40–100 μm are used in sorption methods, which are frequently referred to as solid-phase extraction. Columns or cartridges with such comparatively large particles make it possible to perform sorption at a low pressure, which gives a possibility to use a peristaltic or other low-pressure pump and other simple components of the entire flow system.

The efficiency of a column can be improved due to a decrease of the size of grains because, in the case of finer grained sorbents, the total surface area and hence the phase contact surface is greater and the rate of mass transfer of the analytes between the liquid phase and the sorbent phase is higher [2, 3]. For this reason, materials with a particle size of 2–10 μm are used in columns for high-performance liquid chromatography. The hydraulic resistance of a packed column is inversely proportional to the square of the particle

diameter of sorption material; because of this, a pressure from several hundreds to more than thousand of bars is required with the use of grains smaller than 10 μm in diameter [4, 5]. The application of columns containing a sorbent in the form of suspension (suspension column) in place of packed columns is of interest; on the one hand, this will make it possible to operate with finer grained sorbents and, on the other hand, to avoid the use of pumps, valves, and high-pressure lines. A pressure differential across a suspension column should be considerably lower than that across a packed column.

The sorbent in the form of suspension can be used only if it is retained in the column in the flow of a liquid phase without the use of filters, in the presence of which a packed layer is formed from the suspension, as it takes place on the preparation of sorption and chromatographic columns [4, 5]. This problem can be solved if the particles of a suspension are retained in the limited volume of a flow system due to the action of an external force field (hydrodynamic, thermal, acoustic, etc.). These fields are used for the separation of particles in field flow fractionation methods [6], which are based on the different retention of particles with different size and density. Upon the complete retention of the particles in the separating volume of

the flow system under the action of a force field, conditions can be created under which dissolved analytes sorbed on the selected sorbent particles rather than the particles themselves are separated in the form of the retained suspension. It is also important that the retained particles should not form aggregates; that is, the particles should be distributed and structured in the column volume; in this case, the resulting structures should be reproducible.

In addition to the possibility of using sorbent grains several microns in size at a low pressure, suspension columns are characterized by an additional advantage. In contrast to classical packed columns, the suspended grains of sorbents make it possible to operate with samples containing soluble high-molecular-weight substances and colloidal particles. Biotechnological methods in which sorbent grains are transferred into a suspension due to the ascending flow of a solution containing target components are known [7]. As compared with a packed layer, it is possible to work with macromolecules that penetrate through a sorbent layer due to an increase in the porosity of the sorption system, as demonstrated based on the example of the isolation and separation of proteins. However, the sorbent grains based on modified metal oxides used previously [7] had a very large size (70 μm).

Ultrasonic irradiation is successfully used in analytical chemistry for both sample preparation and the detection of dissolved analytes [8, 9]. Acoustic fields are used much more rarely in the separation and analysis of particles, although this area seems promising for inorganic and bioorganic analysis [10, 11]. The combination of an ultrasonic source and a corresponding flow system made it possible to develop procedures for the separation of inorganic and polymeric particles, which are partially or completely retained in the field of a standing ultrasonic wave. In contrast to the majority of flow fractionation methods, in which the external force field vector is directed perpendicularly to the flat separating channel [6, 7], the field acts along the axis of a separating mini chamber or column in acoustic methods [10–12].

It is also well known that the ultrasonic action can influence the kinetics of sorption of metals from aqueous solutions by complex-forming and ion-exchange materials, which are used in analytical chemistry and technology [6, 8]. The microacoustic flows formed in an ultrasonic field create necessary conditions for the accelerated sorption because of the intensification of mass transfer in the sorbate–sorbent system.

Thus, the ultrasonic field can play two roles in sorption processes: to retain small sorbent grains in a cell or low-pressure column and to simultaneously accelerate the sorption process. The latter circumstance can be important upon going from a packed column to a suspension column with larger porosity, that is, with greater distances between sorbent grains in view of the possibility of the appearance of kinetic problems. The application of ultrasonic fields in a noncavitating

megahertz range seems most promising. This gives the possibility to form the layers of sorbent particles with the periodicity of a half of the ultrasonic wavelength.

In this work, we demonstrated the applicability of suspension columns with small sorbent grains to the extraction of elements from the samples of natural wines, whose organic components do not allow one to perform direct analysis with the application of analytical methods that use argon plasma as an emission source (inductively coupled plasma atomic emission spectrometry) or ion source (inductively coupled plasma mass spectrometry, ICP MS), which received wide acceptance in recent years. Preliminary experiments showed that, in the analysis of white wines, the samples should be diluted by a factor of at least 10 for producing a steady-state argon plasma. However, the concentrations of rare-earth elements and Y in the test samples are such that the reliable direct determination of only some light rare-earth elements can be performed after dilution. In connection with this, sample preparation is required, which includes the separation and, if necessary, preconcentration of analytes with the partial or complete separation of the above components.

The complexity of the identification of wines is caused by many factors: agricultural engineering, soil, grape species, processing technology, and the compositions of auxiliary materials used. Based on the concentrations of trace elements, it is possible to perform the territorial identification of the initial winemaking material, which in many respects determines the price and quality of wines [13–16]. This identification or the establishment of the profile of a test sample of wine is possible based on the concentrations of marker elements (rare elements) because different artifacts can exert noticeable effects on the concentrations of the widespread elements. Methods for the sample preparation of wines were considered elsewhere [15, 17]. It was shown that, in the determination of trace amounts of metals in wines with the use of methods based on the application of inductively coupled plasma, sample preparation is required with the dilution of a test sample (its mineralization or acidic treatment, frequently, in an autoclave). In view of the low concentrations of the rare-earth elements, their preliminary separation and concentration [17] can be required for the determination; this can be performed with the application of sorbents.

Such sorbents include modified silica gels containing iminodiacetate groups, which were successfully used [18, 19] for the extraction of Fe, Cu, Mn, Ni, Co, Zn, Cd, and Pb from different aqueous solutions with the use of packed columns with the grains about 100 μm in size. Based on these results, we demonstrated the applicability of a sorbent of the above type to the extraction of a large number of elements, including the rare-earth elements, from different waters with the use of an ultrasonic suspension column

[10]. For the above reasons, the size of sorbent grains was much smaller (about 6 μm).

In this work, we studied the sorption properties of a sorbent of this type (Diasorb-130-IDK) with respect to the rare-earth metals in order to use it for the extraction and the subsequent determination of the rare-earth elements in wine.

EXPERIMENTAL

Reagents and solutions. In the study of sorption and desorption, a Diasorb-130-IDK sorbent Series 193/I with a grain size of 6 μm was used; the capacity of the sorbent for Cu was 0.2 mg-equiv/g (ZAO BioKhim-MakST, Moscow). For studying sorption from aqueous solutions, metal solutions with a concentration of 0.4 mg/L were used, which were prepared from an ICP-MS-68A Solution A (10 mg/L in 2% HNO_3) (High-Purity Standards, the United States). A 1 M solution of HNO_3 (suprapur nitric acid 65%, Merck, Germany) was used as an eluent. A 25% aqueous solution of ammonia solution (1 : 1) (high purity aqueous ammonia 23-5, GOST [State Standard] 24147-80, Komponent-Reaktiv) was used for adjusting pH.

The test material was Chantarel 2010 (Chardonnay) white dry table wine from Languedoc-Roussillon, France. The initial pH was 3.5.

Equipment. The sorbent sample was weighed on a Highland electronic laboratory balance (HCB 602H, Adam Equipment Co Ltd., the United Kingdom). An orbital shaker (SkyLine, Riga, Latvia) was used for sorption in the batch mode; a CM-6M laboratory centrifuge (SkyLine, Riga, Latvia) was used for the separation of the sediment. The acidity of solutions was measured on an Ekotest-2000 liquid analyzer (NPP Ekoniks). An L/S Master Flex series peristaltic pump (Cole-Parmer, the United States) and an ultrasonic unit (Institute of Analytical Instrumentation, Russian Academy of Sciences, St. Petersburg) were used for passing a solution through the sorption flow system. The yield of sorbent particles from the system was detected with a UV-Vis spectrophotometric flow detector (Institute of Analytical Instrumentation, Russian Academy of Sciences, St. Petersburg).

The system with a focused ultrasonic source (frequency, 2.65 MHz; sound intensity, 10 W/cm^2) was used; a cylindrical flow chamber (volume, 1 mL) was arranged at a distance of 20 mm from the source to ensure the highest efficiency of the force action of ultrasound. The flow chamber was thermostatically controlled with water, which was supplied into a jacket. Water that washed the flow chamber and the radiating surface of the source was withdrawn to remove heat released by ultrasound.

Preparation of the sorbent. A UZG13-0.1/22 ultrasonic generator (VNIITVCh) was used for degassing wine and water before the sorption of metals in the dynamic mode; a Sappfir ultrasonic bath (ZAO PKF-

Sappfir) was used for the disaggregation of a sorbent suspension. Before the introduction of a sorbent into a suspension column (20 mg), it was placed in a 10-mL glass test tube, and 5 mL of twice-distilled water was added; the contents were processed in the ultrasonic bath.

Effect of ultrasound on the sorbent. For studying the behavior of the sorbent under the action of an ultrasonic field, the sorbent was treated with ultrasound for 30 s, 3, and 10 min. For studying the stability of the sorbent suspension to aggregation in ultrasound, a laser analyzer for measuring particle size with a dispersion unit in a liquid medium (ANALYSETTE 22 NanoTec plus, Fritsch, Germany) were used.

Retention of particles in the ultrasonic suspension column. For determining the maximum weight of sorbent retained in the suspension column under the action of an ultrasonic wave, a series circuit of the suspension column with a spectrophotometric detector (at $\lambda = 254 \text{ nm}$) was implemented. The graphs obtained were processed with the aid of the KhromP software (Institute of Analytical Instrumentation, Russian Academy of Sciences, St. Petersburg).

Preparation of the samples of wines by acidic decomposition. Concentrated HNO_3 (10 mL) was added to a 10-mL sample of wine, and the contents were stirred and evaporated to dry residue at 90°C during 10 h. The dry residue was dissolved in 10 mL of 2 M HNO_3 , and the rare-earth elements and Y were determined by ICP MS.

Wine sample preparation by dilution. The samples of wine were diluted by a factor of 10 with a 2% solution of HNO_3 .

Extraction of metals in the batch mode. From 20 to 250 mg of the sorbent was placed in a 50-mL graduated test tube, and 10–50 mL of wine was added; the required acidity was adjusted by the addition of ammonia solution. Then, the test tube was agitated on a shaker for 10 min. A centrifuge (3000 rpm) was used for the separation of solution from the sorbent; a 5-mL portion of the filtrate was taken for elemental analysis by ICP MS. For washing the sorbent, from 10 to 50 mL of twice-distilled water was added to the test tube depending on the sorbent weight, and all of the operations were repeated with the use of the shaker and centrifugation. For the desorption of metals, 5 mL of a 1 M HNO_3 solution was added to the test tube with the sorbent; the contents were shaken for 10 min and then centrifuged, and the filtrate was sampled for ICP MS analysis.

Extractions of metals in the ultrasonic suspension column. Figure 1 shows a schematic diagram of the system. A new principle of fractionating liquid disperse systems—the selective retention of microparticles by an ultrasonic field generated in the flow of a liquid medium—was implemented in the system. The ultrasonic field is generated in a flow chamber, and it serves as a bulk-controlled filter, which is responsible

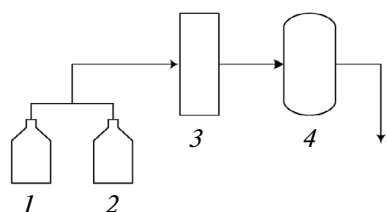


Fig. 1. Schematic diagram of the sorption extraction of metals with the use of a flow ultrasonic suspension column: (1) an analyte, (2) an eluent, (3) a peristaltic pump, and (4) a suspension column.

for the selective retention of particular microparticles depending on their characteristics and field parameters. The volume of the sorption chamber was 1 mL.

Determination of the rare-earth metals. The determination of the rare-earth metals in the obtained solutions was carried out on an X-7 inductively coupled plasma mass spectrometer (Thermo Electron, the United States). The determination was performed at the following operating parameters of the mass spectrometer: generator output power, 1250 W; a PolyCon concentric sprayer; a conical quartz spray chamber cooled to 3°C; plasma-forming argon flow rate, 13 L/min; auxiliary argon flow rate, 0.90 L/min; argon flow rate in the sprayer, 0.98 L/min; and test sample flow rate, 0.8 mL/min. The elements were determined in the samples with the use of solutions containing from 1 to 500 µg/L of reference elements.

Indium was used as an internal standard in the measurements. The limit of detection (LOD) was calculated from the standard formula $LOD = 3\sigma$, where σ is the standard deviation of the background signal of the test element. As a supporting electrolyte, a 2% solution of HNO₃ (the direct measurement of wine samples after dilution) or reference samples (in the course of decomposition or preconcentration) were used. The LOD of the most abundant isotope was used in the subsequent calculations for the elements formed by several isotopes. The LODs thus evaluated for heavy rare-earth elements were 0.001 mg/L and 0.03 µg/L for La, Ce, and Nd.

The relative standard deviation for all of the elements did not exceed 0.3 in the determination of to 5 LODs of these elements, and it did not exceed 0.15 in the measurement of > 5 LODs.

RESULTS AND DISCUSSION

Earlier [11], the retention of sorbent particles in the ultrasonic suspension columns was described and basic recommendations were developed for the construction of new columns with the retention of a greater sorbent mass than that achieved in our previous work [10] with the use of an ultrasonic field. Taking into account these recommendations, we prepared a column with a length of 13 mm and an inside diam-

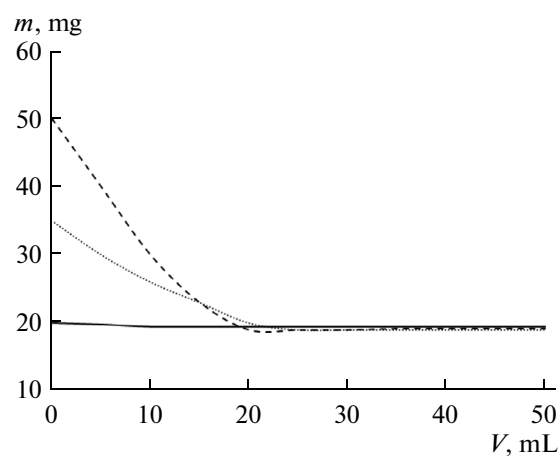


Fig. 2. Retention of a sorbent with mass m at different solution volumes passed at a flow rate of 1 mL/min. Sorbent mass m , mg: (—) 20, (...) 35, and (---) 50.

eter of 8 mm. For this column, the retention of a sorbent in a flow of solution was studied and experiments on the sorption of the elements from the test samples of water and wine were carried out. Figure 2 illustrates the retention of particles of different masses in the flow suspension column. As can be seen, a sorbent with a mass of 20 mg was completely retained in the column used.

The sorbents used in the ultrasonic suspension columns should be stable to aggregation in an ultrasonic field. Earlier, it was found that some sorbents undergo aggregation in an ultrasonic field with time [20]. The aggregation of a sorbent in the suspension columns can lead to a decrease in the efficiency of extraction of the substances and the subsequent deposition of large sorbent particle aggregates in the column. The chosen Diasorb-130-IDK sorbent was tested for particle aggregation in the ultrasonic field; its stability to aggregation in time was found (Fig. 3). As the time of the treatment of a sorbent suspension was changed from 30 s to 10 min, the average particle size (6 µm) remained almost unchanged. This makes it possible to work with the sorbent without fearing for a noticeable change in the size of its grains in the process of use in the ultrasonic column. After the estimation of the sorbent mass quantitatively retained in the column and the testing of its stability to aggregation in the ultrasonic field, the selected sorption material can be recommended for experiments on the sorption of the elements.

The sorption efficiency of the proposed column with 20 mg of a sorbent was evaluated in experiments on the extraction of the rare-earth elements from standard aqueous solutions (Table 1). The experimental data are indicative of the quantitative extraction of the rare-earth elements and yttrium with the use of the proposed ultrasonic suspension column containing 20 mg of the Diasorb-130-IDK sorbent.

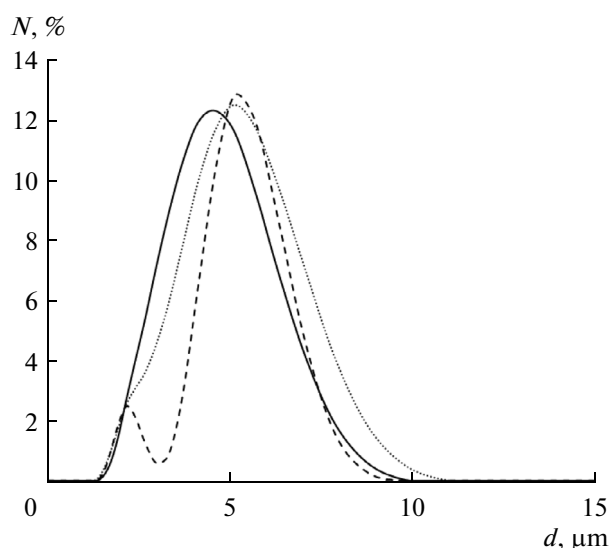


Fig. 3. Sorbent particle size distribution (N , %) with the diameter d after ultrasonic treatment for (...) 1 s, (—) 30 s, and (---) 3 min.

The need for a more complicated sample preparation procedure for wine samples was demonstrated by ICP MS analysis with the use of a sample dilution method with a 2% solution of HNO_3 by a factor of 10 with the application of a suspension column and some other methods. Even at this minimum degree of dilution, the concentrations of a number of elements (Y, Eu, Tb, and Tm) are lower than the LODs and the other rare-earth elements are determined with high errors because of their low concentrations.

The subsequent experiments were carried out with the use of dynamic sorption and desorption in the ultrasonic suspension column and also with the application of batch sorption with the same sorbent and the acidic decomposition of wine samples before their determination by ICP MS. The dynamic version of the sorption extraction and preconcentration of the rare-

earth elements in traditional columns packed with grains of size about $6 \mu\text{m}$ at a low pressure cannot be implemented.

The used method of acidic decomposition implies the destruction of the organic matrix of wine in HNO_3 on boiling. A disadvantage of this method is the resinification of undecomposed organic matter in the course of the evaporation of the mixture; this method is time-consuming and labor-intensive. This sample preparation method takes about 10 h. Nevertheless, the analysis of wine with the use of acidic decomposition makes it possible to estimate the accuracy of results by a comparison with the data obtained with the application of sorption (dynamic and batch) sample preparation methods (Table 2).

In the development of a sample preparation method based on the batch sorption and desorption of the rare-earth elements before their ICP MS determination, we studied the dependence of the experimental results on the mass of the Diasorb-130-IDK sorbent. The mass was varied from 20 to 250 mg, the sample acidity was adjusted to pH 7, and desorption was performed with the use of a 1 M solution of HNO_3 . It was shown that the results of the determination of the elements comparable with the data obtained after the acidic decomposition and dynamic separation of analytes in the suspension column were reached at a sorbent mass of 250 mg (which indirectly evidenced the quantitative extraction of the rare-earth elements at the stage of sample preparation). The disadvantages of the batch mode, as compared with the dynamic mode, are well known: high labor intensity and problems with automation. Sample preparation with the application of a batch method takes about 1 h.

The dynamic version with the application of an ultrasonic suspension column was implemented under the same conditions as the batch method. The same Diasorb-130-IDK sorbent with an average grain size of about $6 \mu\text{m}$ was used; the pH of the initial wine sample was 7, and elution was performed with a 1 M solu-

Table 1. Recovery (R , %) of the metal(III) ions from a standard aqueous solution with a concentration of 0.4 mg/L of each particular element (pH 7.3, $m = 20 \text{ mg}$) in the dynamic mode from a 10-mL sample with the use of the suspension column ($n = 5$, $P = 0.95$)

Metal	R , %	Metal	R , %	Metal	R , %
Y	98	Sm	98	Ho	97
La	97	Eu	99	Er	96
Ce	100	Gd	97	Tm	97
Pr	98	Tb	98	Yb	98
Nd	96	Dy	99	Lu	97

Table 2. Results ($\mu\text{g/L}$) of the mass-spectrometric determination of the rare-earth elements in Chantarel 2010 (Chardonnay) white wine (France) with the use of different sample preparation methods (volume, 10 mL)

Metal	Acid decomposition ($n = 5, s_r = 0.10\text{--}0.15$)	Batch sorption ($n = 6, s_r = 0.10\text{--}0.15$)	Dynamic sorption ($n = 6, s_r = 0.08\text{--}0.11$)
Y	0.275	0.222	0.226
La	0.018	0.015	0.017
Ce	0.360	0.220	0.230
Pr	0.073	0.061	0.072
Nd	0.183	0.201	0.223
Sm	0.080	0.069	0.075
Eu	0.044	0.036	0.040
Gd	0.060	0.062	0.067
Tb	0.044	0.042	0.048
Dy	0.068	0.070	0.072
Ho	0.035	0.028	0.032
Er	0.060	0.053	0.055
Tm	0.033	0.030	0.033
Yb	0.069	0.063	0.064
Lu	0.033	0.023	0.027

tion of HNO_3 . As compared with the batch sorption sample preparation procedure, the difference was in the mass of the used sorbent (20 mg instead of 250 mg), the times of sorption/desorption stages (25 min instead of 1 h), and a more convenient flow method for the separation of the elements before their determination by ICP MS. The accuracy of the obtained results was confirmed by the satisfactory repeatability of data obtained with the application of the dynamic and batch sorption separation of analytes and a fundamentally different sample preparation method based on the preliminary acidic decomposition of the samples of wine (Table 2). The reproducibility of the results for the dynamic method was somewhat better in comparison with the other two sample preparation methods.

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