ISSN 1061-9348, Journal of Analytical Chemistry, 2017, Vol. 72, No. 6, pp. 608–616. © Pleiades Publishing, Ltd., 2017.
Original Russian Text ©A.V. Malkov, A.Yu. Kozhevnikov, D.S. Kosyakov, A.E. Kosheleva, 2017, published in Zhurnal Analiticheskoi Khimii, 2017, Vol. 72, No. 6, pp. 521–529.

Determination of Ni, Co, and Cu in Seawater by Total External Reflection X-Ray Fluorescence Spectrometry

A. V. Malkov, A. Yu. Kozhevnikov, D. S. Kosyakov*, and A. E. Kosheleva
Lomonosov Northern (Arctic) Federal University, Arkhangelsk, 163002 Russia
**e-mail: d.kosyakov@narfu.ru*

Received September 16, 2016; in final form, November 18, 2016

Abstract—Total external reflection X-ray fluorescence spectrometry is a promising method for the highly sensitive determination of heavy metals in seawater, offering such advantages as the mobility of the used equipment and the low cost of analysis. Various methods of sample preparation to the analysis of seawater aimed at the elimination of interferences with the salt matrix were compared. It was shown that the method based on the preliminary extraction of metals as diehyldithiocarbamate complexes followed by back extraction is characterized by the highest efficiency. A procedure was developed for the determination of Ni, Cu, and Co in seawater with limits of detection at a level of 0.16–0.26 μg/L.

Keywords: total external reflection X-ray fluorescence spectrometry, heavy metals, seawater, sample preparation, back extraction

DOI: 10.1134/S1061934817060107

Because of a high toxicity of heavy metal ions, their determination in environmental samples is one of the most important problems of environmental monitoring [1]. Taking into account an increasing interest of researchers in the problems of human impact on the ecosystem of seas and oceans, seawater deserves special attention as an object of monitoring. Heavy metals are present in seawater in extremely low concentrations against a background of a complex salt matrix and organic substances of different classes; therefore, their determination is a complex analysis task [2, 3]. The methods of analysis must satisfy such requirements as high sensitivity (low limit of detection) and selectivity [2].

At present the problem is solved using methods of stripping voltammetry (**SVA**), electrothermal atomization atomic absorption spectrometry (**ETAAS**), and inductively coupled plasma atomic emission spectrometry and mass spectrometry (**ICP AES** and **ICP MS)** [4].

The ETAAS and ICP MS techniques possess the best characteristics and ensure the attainment of limits of detection for the majority of heavy metals at a level of 0.01 μg/L [5–7]. However, the problems of matrix effects in the analysis of seawater by the specified methods have not been solved yet, and the complexity of the used equipment and cost of analysis remain high.

Total external reflection X-ray fluorescence spectrometry (**TXRF**), finding more and more wide application to the highly sensitive elemental analysis of various objects [8], can be a state-of-the-art alternative to the above methods. The sensitivity of the method is comparable to that of ICP AES [9] and, in contrast to AAS, this method is multielemental and ensures the simultaneous determination of concentrations of several dozens of components in one sample. Among the important advantages of TXRF, making it especially promising for field research, are small dimensions and weight of the equipment, low energy consumption, and low cost of analysis. The last factor is determined by the fact that all operations are done with the smallest amounts of test samples (from hundreds of microlitres to several milliliters) and reagents, and consumables are virtually not required for the work of equipment. The physical basics and scopes of TXRF were considered in detail in review [9].

The application of this method to the analysis of natural waters [9–12], including seawaters, was described in [13–15]; numerous publications were devoted to the use of TXRF for the study of drinking, mineral, waste, and other waters [16–29].

The application of TXRF to the determination of heavy metals in seawaters is undoubtedly promising and offers certain advantages over other methods. However, a number of the problems dealing with the preparation of samples with a salt matrix must be solved. Thus, to improve the signal-to-background ratio, some authors used sample dilution in the ratio up to 1000, which led to a considerable decrease in the sensitivity of analysis [10]. Approaches to sample preparation based on the separation of analytes from the matrix seem to be more promising. Samples are prepared using different versions of sorption preconcentration [4, 30, 31], and also the extraction of metal ions with organic solvents as complexes [32–34]. In procedure [35], it was recommended to use an approach ensuring the extraction of a number of metals from seawater with tetrachloromethane as diethyldithiocarbamate complexes, followed by back extraction to nitric acid and determination by ETAAS. Along with the removal of salts, such preparation includes preconcentration, which significantly lowers the limits of detection for analytes.

In this work, we set a problem of the development of a methodology of the highly sensitive determination of heavy metals in seawater with using TXRF on the basis of the search for and improvement of methods of sample preparation focused on the elimination of matrix effects.

EXPERIMENTAL

Test samples. The test samples were samples of surface seawater collected in the Barents Sea during field works in 2015. Directly after their selection, samples were preserved by acidification with nitric acid to pH 1–2.

Equipment. To determine the concentration of heavy metals, we used an S2 Picofox total external reflection X-ray fluorescence spectrometer (Bruker, Germany) in the modification with a high-efficiency module and automatic sample loading. The X-ray tube with a maximum power of 37 W (50 kV, 750 μA) with a Mo anode, equipped with a multilayered Ni/C monochromator, was an excitation source (energy 17.5 keV). A silicon drift detector with a thermoelectric cooling area of 30 mm^2 was used. The maximum counting rate was more than 100000 pulses/s and power resolution, <150 eV at the MnK_α line.

Preparation of solutions. We used prepurified 1% solutions of sodium *N,N*- diethyldithiocarbamate and an acetate buffer solution of pH 5.4 to obtain metal complexes. The purification procedure was similar to that described in [35].

Standard solutions were prepared with using certified reference materials of the composition of metals (**GSO** series), by diluting aliquot portions taken with micropipettes to volumetric flasks with deionized water. Deionized water of the resistivity 18.2 MΩ cm was obtained on a Simplicity UV system for the preparation of ultrapure water (Millipore, Germany). Standard solutions were stabilized by acidification with conc. high-purity HNO_3, predistilled without boiling on a DST-1000 apparatus (Savillex, United States).

The internal standard was a Ga solution for ICP (Panreac, Reference standards acc. NIST CRM 3119a) of the concentration 1.000 ± 0.002 g/L.

Metal complexes were extracted with tetrachloromethane "for spectroscopy" (Komponent reactive, Russia) and used without additional purification.

Determination of metal concentrations. A 10-μL portion of a sample containing 50 μg/L of the internal standard was placed on a quartz sample holder with a micropipette and dried on a warm plate with a surface temperature of 65 ± 1°C for 300 ± 5 s. The volume of the organic phase in the case when it was placed on the holder was 15 μL.

Fluorescence intensity was measured within 1200 s at an accelerating voltage across the X-ray tube 50 kV and current 600 μA. The spectrum obtained was automatically processed by the spectrometer software (Spectra7, Bruker) using the Profile Bayes (normal fit) deconvolution mode. The concentrations of elements in the prepared sample were calculated by the internal standard method; recalculation to the concentration in the initial sample depended on the method of sample preparation.

Sample preparation to the direct determination of metals. A sample of seawater was filtered through a membrane filter (syringe cap) with a pore diameter of 0.25 μm (Millex-GN, Millipore, Germany). Seawater (800 μL) was mixed with a standard Ga solution of the concentration 250 μg/L (200 μL) in a polypropylene microcentrifuge tube using a vortex within 60 s. Metal concentration in the sample was calculated by multiplying the found concentration (taking into account blank sample) by the dilution coefficient, equal to 1.25.

In the determination of metals in diluted seawater, 50 μL of seawater was similarly mixed with 750 μL of deionized water and 200 μL of a standard Ga solution of the concentration 250 μg/L. The dilution coefficient in this case was equal to 20.

Extraction of metals. The procedure for the extraction of metal complexes from seawater [35] was modified to minimize the volume of the sample necessary for analysis. Extraction was performed in polypropylene microcentrifuge test tubes of the volume 1.5 mL. An 1-mL portion of a sample was mixed with 100 μL of an acetate buffer solution and 50 μL of a sodium diethyldithiocarbamate solution, 100 μL of tetrachloromethane was added to the test tube, and extraction was performed within 5 min by stirring with a vortex. Then 15 μL of the lower organic layer (extract) was taken from the test tube with a micropipette and placed in a sample holder. Metal concentrations in this version of procedure were not calculated, the repeatability of the results was assessed by fluorescence intensity.

Back extraction of metals. Extraction was performed in polypropylene microcentrifuge test tubes of the volume 1.5 mL. One milliliter of a sample was mixed with 100 μL of an acetate buffer solution and 50 μL of a solution of sodium diethyldithiocarbamate, 200 μL tetrachloromethane was added to the test tube,

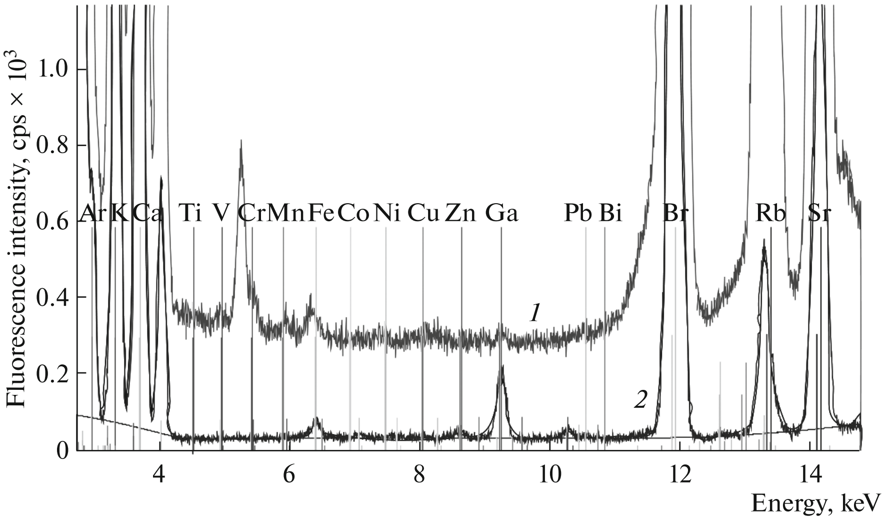

Fig. 1. A fragment of an X-ray fluorescence spectrum of (*1*) seawater and (2) seawater diluted 20-fold.

and extraction was performed within 5 min under stirring. Then 150 μL of the lower organic layer (extract) was taken from the test tube and transferred to a 0.2-mL microcentrifuge test tube, 4 μL of conc. HNO_3 was added, and the mixture was stirred again within 5 min. Metal complexes decomposed and were transferred into nitric acid (back extraction). After adding 76 μL of an internal standard solution (Ga, 50 μg/L), an aliquot portion of the back extract (upper layer in the test tube) was placed in a sample holder and dried. The concentration of metals in the sample was calculated by multiplying the found concentration by the concentration factor, previously determined for each element using a series of standard solutions.

RESULTS AND DISCUSSION

Direct determination of metals. The simplest version of sample preparation to TXRF is the direct dosing of a sample of seawater on a sample holder followed by drying. An example of a fluorescence spectrum obtained by this method is shown in Fig. 1 (curve *1*). One can see that the level of background signal due to the scattering of X-radiation is very high. Intense scattering is due to the formation of a thick layer of a dry residue (salt) on the surface of sample holder in drying the sample. In addition to the high intensity of the background signal, we observed its strong oscillations. As a result, the signal-to-background ratio for the spectrum recorded under such conditions was extremely unfavorable, which resulted in high values of the limit of detection.

To improve the signal-to-background ratio, we selected the multiplicity of dilution. The acceptable level of background scattering (integrated intensity of background under the GaK_α line below 5000 pulses/s) was attained at sample dilution by 10–20 times. Figure 1 presents a spectrum of a sample of 20-fold diluted seawater (curve *2*) with an addition of an internal standard (Ga). In the fluorescence spectrum recorded under such conditions, line resolution was improved and the level of signal background was decreased significantly. However, the intensity of lines of characteristic radiation of sample elements was low, which in combination with dilution resulted in unacceptably high values of the limit of detection for heavy metals. Thus, for iron and lead, the limits of detection were 70 and 50 μg/L at maximum permissible concentrations of 50 and 10 μg/L, respectively. In [10], the limit of detection for manganese in seawater (400 μg/L and more) was reported at a multiplicity of dilution from 1 to 1000. Because of the unfavorable signal-to-background ratio, the reproducibility of the results of the determination of trace amounts of elements remained low.

Therefore, we can conclude that the direct determination of metals even with dilution can be used only for the determination of macrocomponents in seawater; trace amounts of heavy metals cannot be determined by this method. This conclusion agrees with the results of work [10].

Determination of heavy metals using extraction. We used metal extraction as chelate complexes to eliminate the effect of the salt matrix.

In TXRF, it is important that the product of metal preconcentration is in the liquid phase or can be easily transferred to it. From this viewpoint, the most promising method of separation is the extraction of metal complexes to an organic solvent. An important advantage of extraction is the short duration of the separation procedure, which improves the rapidity of the whole analysis.

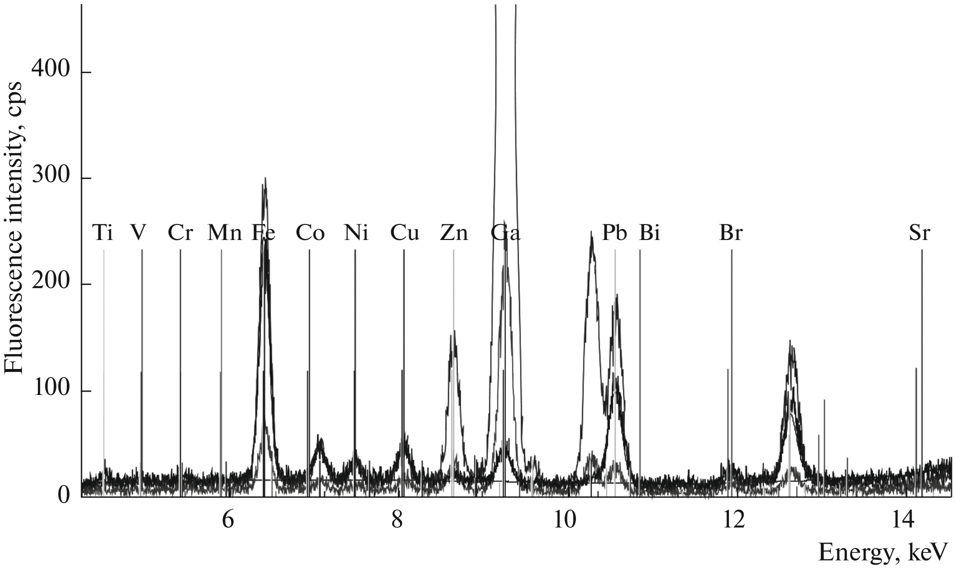

Fig. 2. A fragment of a fluorescence spectrum of an organic extract (results of three replicate determinations).

A combination of advantages of the extraction separation of the components of seawater with the X-ray fluorescence determination of metals seems to us promising. An analysis by TXRF requires several dozens microlitres of a sample. Therefore, the volume of the analyzed water can be reduced from 500 mL [35] to 1 mL. In this case, preconcentration is performed by liquid—liquid microextraction.

To simplify the procedure of sample preparation, it seemed expedient to directly apply the organic extract onto the sample holder. However, this arose a number of methodological difficulties. As can be seen in Fig. 2, fluorescence intensity in this case varied over a wide range even for replicate measurements. The reason for the instability of the results can be that dosing small volumes of organic solvents (below 15 μL) results in errors in the measuring volume and reduces the reproducibility of dosing. Application of 10–25 μL of an organic phase with low surface tension onto a sample holder led to its spreading outside the central zone of the sample holder. As a result, considerable part of a sample could appear outside the zone of the effective operation of the detector, which resulted in the low reproducibility of the results of measurements. The problem of the low reproducibility of the results in the application of the organic phase onto the sample holder was also noted in the work [18].

Therefore, metal extraction as complexes ensures the elimination of noises due to salt matrix; however, the low reproducibility of the results limits the use of this version of the procedure.

Determination of heavy metals using back extraction. We used back extraction of metals from the organic phase to eliminate the above shortcomings. In this case, in dosing an acid back extract onto the sample holder, the reproducibility of the results remained high (Fig. 3).

Fluorescence spectra of the initial seawater (curve *1*) and of a back extract obtained after sample preparation are shown in Fig. 4 (curve *2*). It is clear that the intensity of background scattering for the back extract is low in comparison to that for the initial water. The intensity of the characteristic lines of elements present in the sample, on the contrary, considerably increases after preconcentration.

The completeness of the reaction of complex formation by metals with chelating agents depends on the pH of solution. The recovery of the analytes was estimated by varying pH in the range from 4.0 to 6.3 because of changes in the composition of the acetate buffer solution (Fig. 5). In our opinion, pH 5.4 was optimum for group preconcentration.

The intensity of characteristic lines in the X-ray fluorescence spectrum of the back extract, except for the properties of the analyte, depends on the completeness of its transition from water to the extract and from the organic phase to nitric acid. Different recoveries of elements make expedient the introduction of an internal standard into the back extract rather than into the initial water. In this case, the concentration of elements calculated by the spectrometer software will correspond to the back extract and, to calculate the concentration of analytes in the sample, one should use recalculation. The recalculation coefficients (concentration factors) for analytes were calculated from the found concentrations of standard solutions with the preset concentration of metals. Standard solutions contained from 2.5 to 250 μg/L of V, Cr(VI), Mn, Fe,

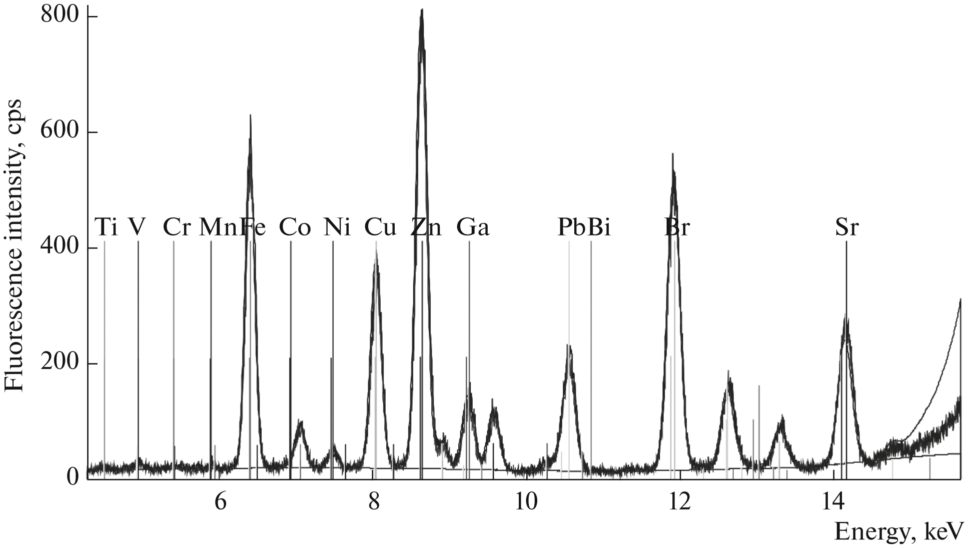

Fig. 3. A fragment of a fluorescence spectrum of a back extract of seawater (results of two replicate determinations).

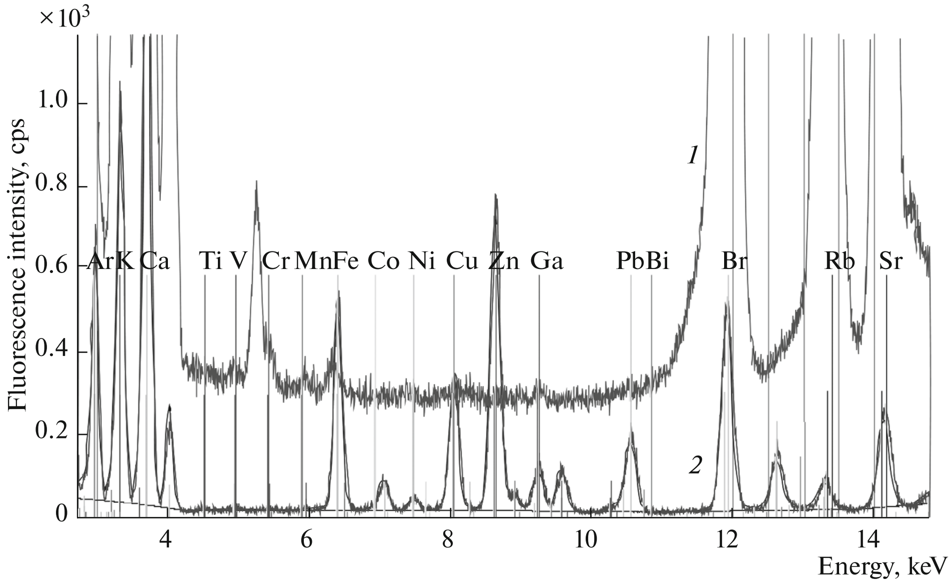

Fig. 4. A fragment of a fluorescence spectrum of (*1*) seawater and (*2*) product of the back extraction of the organic extract with nitric acid.

Co, Ni, Cu, Zn, Cd, Pb, and Bi. The concentration factor was the slope of the dependence of element concentration in the back extract on its concentration in the sample (Fig. 6). For some elements, we observed deviations from direct proportionality (nonzero value of the absolute term in the linear equation). They were due to the presence of traces of these elements on the sample holder and in the solvents (nitric acid and deionized water). These trace amounts could not be eliminated completely [4]; therefore, in quantitative analysis, it was necessary to perform a blank experiment.

Residual amounts of Fe and Zn on the sample holder were rather great and unstable, so that the determination of these elements was insufficiently accurate even taking into account the result of the blank experiment.

Under the conditions of the proposed procedure, chromium gave response only if it was present as Cr(VI); Cr(III) was not preconcentrated as a die-

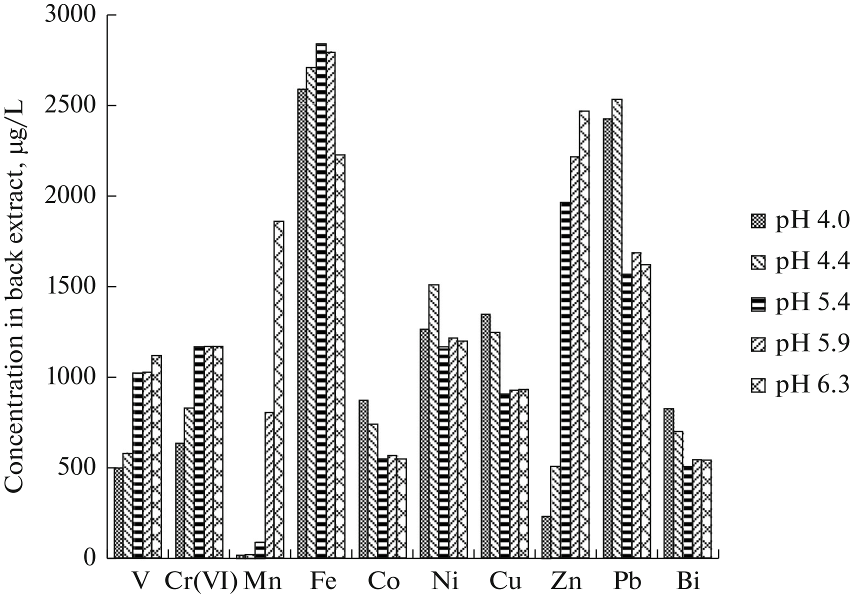

Fig. 5. Effect of pH on the efficiency of metal preconcentration.

thyldithiocarbamate complex. Manganese compounds were also not extracted from water. Concentration factors for Pb and Cd must be additionally refined because of possible interelement effects (of As and K, respectively). Interelement effects were reduced to partial (CdL_α and KK_α) or complete (PbL_α and AsK_α) overlaps of spectral lines. Using back extraction, we could multiply reduce the concentration of alkali and alkaline earth metals in the sample; however, they were not removed completely (the residual concentration of K and Ca was of about 3 mg/L and of Sr, 50 µg/L). Concentration factor for V and Bi under the selected conditions was rather low, which increased the limit of detection for these elements by the above procedure.

Therefore, using of the proposed procedure, one can most efficiently determine Ni, Cu, and Co. The determination must include the preliminary treatment of a sample of seawater, extraction of metal diehyldidithiocarbamate complexes with tetrachloromethane, and back extraction of metals with nitric acid. Preliminary treatment consists in filtering of a sample through a membrane filter and the addition of a complexant solution and a buffer solution for the attainment of the optimum pH value. The water sample is subjected to extraction with tetrachloromethane under stirring, an aliquot portion of the organic extract is taken, and back extraction is performed. Back extraction is performed with nitric acid to which an internal standard (Ga) is added.

The accuracy of the results obtained by the proposed procedure was estimated by the added–found method. The concentration of heavy metals in the sample of seawater (Fig. 7, curve *2*) and in the same sample with an addition of a standard solution with the concentration 50 µg/L (Fig. 7, curve *3*) was found.

The results of analysis of the sample of seawater and seawater with an additive are presented in Table 1. The agreement between added and found amounts of analytes (by the *t*-test for a confidential probability of 95% [36]) can be considered satisfactory. The limits of detection for elements taking into account preconcentration at the step of sample preparation (Table 1) were calculated for samples of seawater using the spectrometer software.

The results of statistical processing of the obtained experimental data for a series of eight replicate determinations are presented in Table 2. They point to an insignificant scatter of the data: the value of the varia-

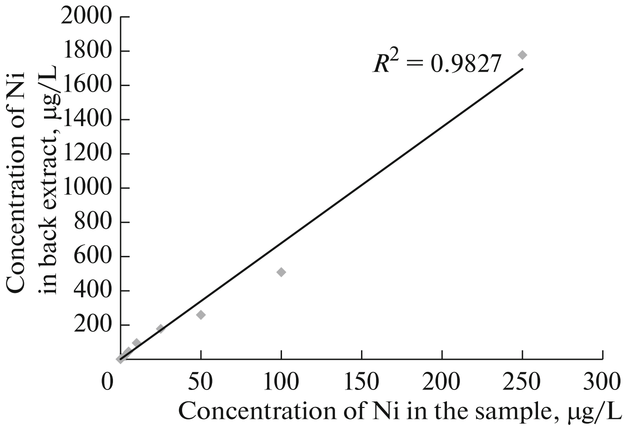

Fig. 6. Calibration dependence for the determination of concentration factor for nickel.

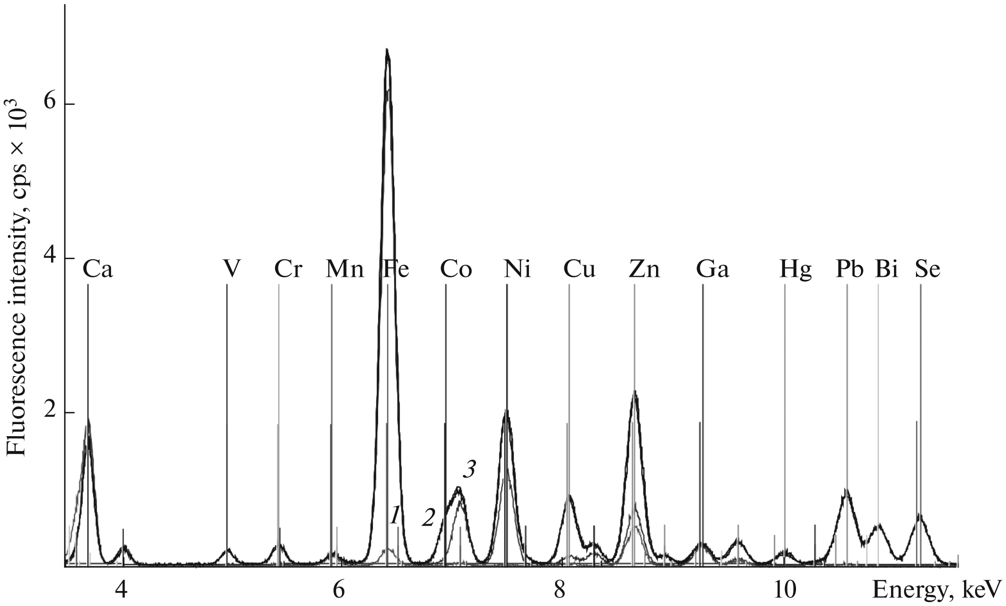

Fig. 7. A fragment of an X-ray fluorescence spectrum of a back extract of seawater (region of excitation energies corresponding to analyte lines): *1,* blank sample; *2,* seawater; *3,* seawater with an additive. Ga and Mn internal standard with the concentration 47.5 μg/L.

tion coefficient did not exceed 33% and the studied set of samples was uniform [37].

The values of the limits of detection we obtained are higher than those for alternative procedures, ICP MS [5] and ETAAS [6], which also included the preconcentration stage. An advantage of the proposed procedure is in a small amount of consumables and reactants used for sample preparation and low energy consumption, which ensures the low cost of single analysis. The procedure can be performed in a mobile (ship) laboratory, which excludes the need in the delivery of samples to a stationary laboratory. The full cycle takes 60 min, which is approximately equal to the time of metal determination by atomic absorption spectrometry.

Table 1. Assessment of the accuracy of the results of analysis*

Metal	Found, μg/L			Limit of detection, μg/L
	seawater	seawater with additive	difference	
V	1.3	46.5	45.2	0.92
Cr(VI)	2.3	40.9	38.6	0.68
Fe	591	647	55	0.36
Co	<0.26	45.98	45.96	0.26
Ni	66.1	117.8	51.7	0.18
Cu	4.75	48.06	43.31	0.16
Zn	39.3	104.1	64.8	0.15
Cd	<3.1	45.20	45.20	3.1
Pb	0.51	40.58	40.07	0.06
Bi	<0.13	44.24	44.24	0.13

* Added 50 μg/L of each metal.

Table 2. Relative error boundaries and coefficients of variation

Element	Relative error boundaries at a probability of $P = 0.95$, $\pm \delta$, %	Coefficient of variation V under the condition of reproducibility, %
Co	11	4
Cu	17	7
Ni	14	6

* * *

Thus, in using total external reflection X-ray fluorescence spectrometry for the determination of the concentration of Ni, Cu, and Co in seawater, the optimum version of sample preparations consists in the extraction preconcentration of metals as diethyldidithiocarbamate complexes followed by back extraction. The proposed approach ensures the determination of the concentration of Ni, Cu, and Co with errors ($n = 8$, $P = 0.95$) 14, 17, and 11% and limits of detection (μg/L) 0.26 for Co, 0.18 for Ni, and 0.16 for Cu, respectively.

ACKNOWLEDGMENTS

We are grateful to the staff of expedition of the project “Arctic Floating University–2015” for the collection of samples.

This work was performed using the instrumentation of the Core Facility Center “Arktika” under financial support of the Ministry of Education and Science of Russian Federation (state assignment project no. 4.2518.2017).

REFERENCES

1. Pilipenko, A.T., Pochinok, V.Ya., Sereda, I.P., and Shevchenko, F.D., *Metally. Obshchie svoistva metallov. Spravochnik po elementarnoi khimii* (Metals. General Properties of Metals. Handbook of Basic Chemistry), Pilipenko, A.T., Ed., Kiev: Naukova dumka, 1985.
2. *Rukovodstvo po metodam khimicheskogo analiza morskikh vod* (Guide to Methods of Chemical Analysis of Sea Water), Leningrad: Gidrometeoizdat, 1977.
3. Alekin, O.A., *Osnovy gidrokhimii* (Fundamentals of Hydrochemistry), Leningrad: Gidrometeoizdat, 1953.
4. *Methods of Seawater Analysis*, Grasshoff, K., Kremling, K., and Ehrhardt, M., Eds., New York: Wiley, 1999.
5. Vegueria, S.F.J., Godoy, J.M., Calixto de Campos, R., and Goncalves, R.A., *Microchem. J.*, 2013, vol. 106, p. 121.
6. Kojuncu, Y., Bundalevska, J.M., Ay, U., Čundeva, K., Stafilov, T., and Akçin, G., *Separ. Sci. Technol.*, 2004, vol. 39, p. 2751.
7. Bruland, K.W., Coale, K.H., and Mart, L., *Mar. Chem.*, 1985, vol. 17, p. 285.
8. Klockenkämper, R., *Total-Reflection X-Ray Fluorescence Analysis*, New York: Wiley, 1997.
9. Alov, N.V., *Zavod. Lab., Diagn. Mater.*, 2010, vol. 76, no. 1, p. 4.
10. Pashkova, G.V. and Revenko, A.G., *Analitika Kontrol’*, 2013, vol. 17, no. 1.
11. Revenko, A.G., *Analitika Kontrol’*, 2010, vol. 14, no. 2, p. 42.
12. Klockenkämper, R. and von Bohlen, A., *Spectrochim. Acta, Part B*, 2014, vol. 99, p. 133.
13. Freimann, P. and Schmidt, D., *Spectrochim. Acta, Part B*, 1989, vol. 44, no. 5, p. 505.
14. Staniszewski, B. and Freimann, P., *Spectrochim. Acta, Part B*, 2008, vol. 63, no. 11, p. 1333.
15. Costa, A.C.M., Anjos, M.J., Lopes, R.T., Perez, C.A., and Castro, C.R.F., X-ray Spectrom., 2005, vol. 34, no. 3, p. 183.
16. Barreiros, M.A., Carvalho, M.L., Costa, M.M., Marques, M.I., and Ramoset, M.T., *X-Ray Spectrom.*, 1997, vol. 26, no. 4, p. 165.
17. Kunimura, S. and Kawai, J., *Anal. Sci.*, 2007, vol. 23, no. 10, p. 1185.
18. Kump, P., Necemer, M., and Veber, M., *X-Ray Spectrom.*, 1997, vol. 26, no. 4, p. 232.
19. Hołynska, B., et al., *Fresenius’ J. Anal. Chem.*, 1998, vol. 362, no. 3, p. 294.
20. Costa, A.C.M., Anjos, M.J., Moreira, S., Lopes, R.T., and de Jesus, E.F.O., *Spectrochim. Acta*, vol. 58, no. 12, p. 2199.
21. Lieser, K.H., Flakowski, M., and Hoffmann, P., *Fresenius’ J. Anal. Chem.*, 1994, vol. 350, p. 135.
22. Stossel, R.P. and Prange, A., *Anal. Chem.*, 1985, vol. 57, no. 14, p. 2880.
23. Mages, M., Woelfl, S., Óvári, M., and Tümplingjun, W., *Spectrochim. Acta, Part B*, 2003, vol. 58, no. 12, p. 2129.
24. Avila-Perez, P., Zarazúa, G., Tejeda, S., Barceló-Quintal, I., Díaz-Delgado, C., Carreño-Leónet, C., *X-Ray Spectrom.*, 2007, vol. 36, no. 5, p. 361.
25. Espinoza-Quinones, F.R., et al., *J. Radioanal. Nucl. Chem.*, 2010, vol. 283, no. 2, p. 465.
26. Margui, E., Tapias, J.C., Casas, A., Hidalgo, M., and Queralt, I., *Chemosphere*, 2010, vol. 80, no. 3, p. 263.
27. Stosnach, H., *Adv. X-Ray Anal.*, 2005, vol. 48, p. 236.
28. Raznomazov, V.M., et al., *Ekol. Prom. Proizvod.*, 2009, no. 4, p. 2.
29. Margui, E., Floor, G.H., Hidalgo, M., Kregsamer, P., Roman-Ross, G., Streli, C., and Queralt, I., *Spectrochim. Acta, Part B*, 2010, vol. 65, no. 12, p. 1002.
30. *M-049-V/03* (Methodology)*: Method for Performing Measurements of the Mass Concentration of Vanadium, Bismuth, Iron, Cobalt, Manganese, Copper, Nickel,*

Lead, Chromium, and Zinc in Potable, Natural, and Waste Waters by X-Ray Fluorescent Method after Preconcentration on Cellulose DETATA Filters, St. Petersburg: Spektron, 2003.

31. Zeinalov, R.Z., Tataeva, S.D., and Ataeva, N.I., *Analitika Kontrol'*, 2013, vol. 17, no. 1, p. 89.
32. Mamontova, S.A. and Pchelintseva, N.F., *Zh. Anal. Khim.*, 1979, vol. 34, no. 11, p. 2231.
33. Danielsson, L.-G., Magnusson, B., and Westerlund, S., *Anal. Chim. Acta*, 1978, vol. 98, p. 47.
34. *Metodicheskie ukazaniya po opredeleniyu toksichnykh zagryaznyayushchikh veshchestv v morskoi vode na fonovom urovne no. 45* (Methodological Guidelines no. 45 for the Determination of Toxic Pollutants in Seawater at the Trace Level), Moscow: Gidrometeoizdat, 1982.
35. *RD* (Regulatory Document) *52.10.243-92: Guidelines on the Chemical Analysis of Seawater* (revised versions *RD 52.10.735-2010* and *RD 52.10.739-2010*), Moscow, 1993.
36. Smagunova, A.N. and Karpukova, O.M., *Metody matematicheskoi statistiki v analiticheskoi khimii* (Methods of Mathematical Statistics in Analytical Chemistry), Rostov-on-Don: Feniks, 2012.
37. Sachs, L., *Statistische Auswertungsmethoden*, Berlin: Springer, 1968.

Translated by E. Rykova