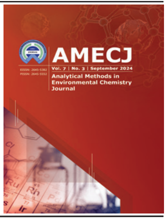
Anal. Methods Environ. Chem. J. 7 (3) (2024) 83-98

Research Article, Issue 3
Analytical Methods in Environmental Chemistry Journal
Journal home page: www.amecj.com/ir



A novel approach to simultaneously determine elements in seawater using total reflection X-ray fluorescence spectroscopy

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ARTICLE INFO:
Received 19 May 2024
Revised form 20 Jul 2024
Accepted 18 Aug 2024
Available online 30 Sep 2024

Keywords:
Trace elements,
Total reflection X-ray fluorescence spectroscopy,
Diethyldithiocarbamate,
Seawater,
Extraction and back-extraction,
Arctic pollution

ABSTRACT

We have applied the modern total reflection X-ray fluorescence spectroscopy (TXRF) method to simultaneously determine the number of elements in seawater. However, seawater contains a large number of salts, so it negatively affects the detection limit of elements and requires a preliminary separation procedure based on liquid-liquid microextraction (LLE) with diethyldithiocarbamate ($NaS_2CN(C_2H_5)_2$) as a chelating agent, and tetrachloromethane as an extractant. We have studied the effect of pH on the separation of elements and proposed an additional stage of sample preparation and mercury stabilization in solution using sodium diethyldithiocarbamate. The calibration curves for 12 elements (V, Cr, Fe, Co, Ni, Cu, Zn, Se, Cd, Hg, Pb, Bi) were obtained. The detection limit of trace elements for Hg, Pb, Zn, Cr, and Cd was achieved from 0.1 to 7 g L^{-1}. The preconcentration factors for selenium (Se) and zinc (Zn) were obtained at 4.25 and 25.1, respectively (recovery more than 95%). This approach has been successfully applied to estimate the content of elements in the seawater of the Arctic region, demonstrating its practical applicability. Metals such as Fe, Zn, Pb, Ni, Cu, Cr, and V were found in seawater samples with RSD below 5%. We found that the concentrations of Cu, Ni, Zn, and Pb correlate with each other and do not correlate with the content of Fe, Cr, and V. The study found that the concentrations of trace elements in seawater are below their maximum permissible concentrations.

1. Introduction

Seawater contains many elements, including those that migrate there due to anthropogenic activity. Information about the distribution of these elements is important for geochemistry and ecology. The first publications on metal distribution in seawater were released in the 1950s of the last centuries, and this topic is still relevant [1]. For example, in 2021, about 200 articles on this topic were published [2, 3]. The studies carried out in hard-to-reach places of our planet, such as the Arctic seas, are especially interesting [4]. The trace elements (heavy metals) content in seawater is relatively low and usually does not exceed 100 μg L^{-1}. The content of elements depends on many factors, such as depth, currents, etc. For example, in the East Sea (Japan Sea), the Mn concentrations in the surface layer (0–50 m) ranged from 0.1 to 0.4 μg L^{-1}, and the Co concentrations ranged from 2.5 to 7.0 ng L^{-1}. The Cu concentrations were higher in the surface layer, from 0.09 to 0.22 μg L^{-1}.

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https://doi.org/10.24200/amecj.v7.i03.318

The concentrations of Cd and Ni were 9–31 ng L^{-1} and 0.11–0.20 µg L^{-1}, respectively [5]. Compared to the background values, the increase in trace element concentrations may indicate anthropogenic pollution. Seawater pollution has a direct negative impact on marine organisms and the ecosystem in general [6]. Trace elements are distinguished by their high toxicity to living organisms in relatively low concentrations and their ability to bioaccumulate and bio-magnify. Almost all heavy metals are involved in biological processes and are part of many enzymes. The most toxic metals include mercury, cadmium, and lead [7]. The most significant threat is the pollution of water by mercury. Mercury has specific properties, such as affinity for sulfur-containing compounds, the ability to form stable methylated compounds, and reducing to metal from these compounds. These factors determine the high migration mobility of mercury in the biosphere and its volatility and toxicity to most living organisms. The interaction of inorganic mercury compounds with benthic microorganisms produces water-soluble, high-toxic organomercury compounds, including methylmercury. Mercury and methylmercury are also found in Laptev Sea surface sediments [8]. Aluminum, arsenic, cadmium, chromium, copper, lead, nickel, and silver are toxic metals that migrate into the marine environment via natural processes and anthropogenic impacts [9]. The determination of all these elements in seawater has its difficulties. On the one hand, the concentrations of metals found in water are deficient. On the other hand, seawater contains many salts, and various organic substances in the water. As a result, the analytical methods are to meet such requirements as high sensitivity (low detection limit) and high selectivity. During the monitoring studies, methods of analysis that allow simultaneous measurement of the content of several heavy metals in the sample are preferable. The atomic absorption spectroscopy method is traditionally used to determine heavy metals in seawater (cold vapor method for determining mercury and electrothermal atomization method for other metals). The methods of atomic emission spectroscopy and mass spectrometry with inductively coupled plasma are also widely used [10]. ICP MS method has the best characteristics and allows achieving detection limits for most heavy metals at 0.01 µg L^{-1} [11]. However, the problem of eliminating matrix effects in analyzing seawater using these methods remains unresolved. The high salts in the sample lead to contamination of the internal communications of the devices and the need for frequent maintenance of the equipment to avoid its quick failure. In addition, the cost of analysis is high because of the complexity of the equipment and the use of a significant amount of expensive consumables (high-purity argon, graphite cuvettes, etc.). The total reflection X-ray fluorescence spectroscopy (TXRF) method might be an alternative to the abovementioned methods [12]. The TXRF method is based on the analysis of the fluorescence spectrum of a sample, usually liquid, that is deposited on a flat substrate (sample holder). The method allows multi-element analysis, also characterized by high selectivity and a wide dynamic range (5...6 orders of magnitude). An essential advantage of the method is the equipment's low power consumption and compactness, so it is possible to analyze the samples in a mobile laboratory near the sampling site [13]. The expensive consumables are not necessary for the analysis. These advantages make it promising to use the TXRF to determine the content of trace elements in natural waters and seawater. Direct analysis of seawater by the TXRF method allows for the determination of the content of elements in concentrations of not less than 0.1 mg L^{-1}, but such sensitivity does not meet the requirements for microelement analysis [14]. Preliminary separation of seawater makes it possible to eliminate the salt matrix and increase the concentration of analytes to determine trace amounts of elements. Such methods as adsorption, electrochemical precipitation, solid-phase extraction, and chromatographic separation of chelate complexes are used for separation and preconcentration [15–22]. We used microextraction preconcentration in the form of diethyldithiocarbamate complexes to determine Ni, Co, Cu, Cd, and Pb. At the first stage of extraction preconcentration, metal complexes are extracted from water into tetrachloromethane; at the second stage (back-extraction), they are destroyed, and the metals pass into nitric acid [23]. Diethyldithiocarbamate can bond with various metals, and this property has been used in analytical chemistry for a long time [24]. This work aims to improve the methodology of determining heavy metals, including mercury, in seawater using the TXRF method and its application to assess the distribution of some aspects in the Arctic seas. To achieve this purpose, we need to determine the conditions of mercury complexation in seawater samples and to study the pH influence on the separation of mercury ions and other elements during sample preparation. Also, we should calibrate elements in seawater and test the proposed approach on actual seawater samples. Finally, we need to assess the content of elements and the correlation of their concentrations in the waters of the Arctic seas.

2. Material and methods

2.1. The object of the study

We used surface water samples from the Kara, Laptev, and East Siberian Sea as the research objects. The samples were obtained during the 2020 expedition on the vessel (Akademik Mstislav Keldysh; AMK 86) during the work on the international program for the study of the Siberian Shelf (ISSS) and scientific educational expedition in Arctic Floating University in 2023. The samples were filtered and preserved by acidification with nitric acid to pH 1-2 immediately after sampling. The program Arc Gis © 10.4.1 for desktop was used for visualization.

2.2. Equipment and reagents

We used a total reflection X-ray fluorescence spectrometer S2 Picofox (Bruker, Germany) in a modification with a high-efficiency module and automatic sample loading to determine the content of heavy metals. The source of exciting radiation was an X-ray tube with a Mo anode equipped with a multilayer Ni/C monochromator (energy 17.5 keV). The maximum power of the X-ray tube was 37 W (50 kV, 750 μA). The detector is a Si drift detector (area of 30 mm^2) with thermoelectric cooling. The maximum counting rate is over 100000 pulses per second, and the energy resolution is <150 eV on the Mn Kα line. sodium N, N-diethyldithiocarbamate (Na-DEDTC) (CAS Number:20624-25-3), and HNO_3 (CAS Number: 7697-37-2) purchased from Sigma, Germany. Tetrachloromethane (Sigma, CAS Number: 56-23-5) was used as a reagent.

2.3. Preparation of solutions

Pre-purified 1% solution of sodium N, N-diethyldithiocarbamate (Na-DEDTC), and the acetate buffer solution with a pH of 3.2-6.3 were used to obtain metal complexes. Diethyldithiocarbamate solution was purified by threefold extraction (25 mL solution with 2.5 mL tetrachloromethane) [10]. The buffer solution was prepared by dissolving ammonium acetate (PA ACS, Panreac) in deionized water and adding glacial acetic acid to a defined pH. pH control was carried out by the pH meter (Econix-Expert 001; Russia) with a combined glass electrode. Solutions with pH 6.3; 5.9; 5.4; 5.0; 4.8; 4.4; 4.3; 4.0; 3.6; 3.2 and an ionic strength 4 mol L^{-1} were obtained. We added 1 mL of 1% dithiocarbamate solution to 100 mL of buffer and extracted it three times with 5 mL of tetrachloromethane for purification. Standard solutions were prepared using the state standard reference samples of metals, and diluting aliquots were selected using micropipettes in volumetric flasks with deionized water. The Simplicity UV water purification system obtained deionized water with an 18.2 M /cm resistance (Millipore, France). For stability, standard solutions were acidified with HNO_3 purists, spectroscopy, grade, and refined by sub-boiling distillation at the DST-1000 system (Savillex, USA). Calibration solutions contained NaCl (35 g L^{-1}) and the specified amounts of metals for seawater modeling. The initial NaCl solution with a concentration of 70 g L^{-1} was previously purified using the same method as the buffer solution. We used Ga solution for ICP (Panreac, Reference standards acc. NIST SRM 3119a) with a concentration of 1.000 ± 0.002 g L^{-1} as an internal standard to establish the precise concentration of calibration solutions. Tetrachloromethane "for spectroscopy" grade was used to extract metal complexes without additional purification.

2.4. Sample preparation

Extraction was performed in polypropylene microcentrifuge test tubes with a volume of 1.5 mL. In the two test tubes, 1200 µL of samples were mixed with 100 µL of acetate buffer and 50 µL of sodium diethyldithiocarbamate solution. 100 µL of tetrachloromethane was added into the test tube, and extraction was carried out for 5 minutes by shaking on the IKA MS3 digital vortex at the frequency of 1500 rpm. We separated the resulting emulsion by centrifugation for 2 minutes on the IKA mini G centrifuge. 80 µL of the lower organic layer (extract) was taken from each test tube and transferred to the 0.2 mL microcentrifuge test tube; 5 µL of HNO_3 was added and shaken again for 5 min. At that point, metal complexes disintegrate and pass into nitric acid (re-extraction). After adding 45 µL of deionized water and stirring, the sample was centrifuged again. Then 25 µL of the re-extract (the top layer in the test tube) was transferred to another test tube of the same volume and mixed with 25 µL of manganese solution (500 µg L^{-1}, internal standard) and 4 µL of sodium diethyldithiocarbamate (mercury stabilizer). 10 µL of the resulting solution was placed in quartz glass sample holders by micropipette and dried on a heating panel with a surface temperature of 65 ± 1 ° C for 300 ± 5 seconds or in a vacuum desiccator for 20 minutes. Thus, the sample preparation included the following stages, shown in the diagram (Fig. 1). At stage 1 of the process (extraction), the concentration of elements should increase 12 times. At stage 2 of the process (re-extraction), the concentration of elements should increase by 3.2 times. Thus, the overall theoretical preconcentration factor should be 38.4. We performed from 4 to 6 parallel measurements for each solution. The blank sample (deionized water that has passed all stages of sample preparation, including acidification) was analyzed ten times.

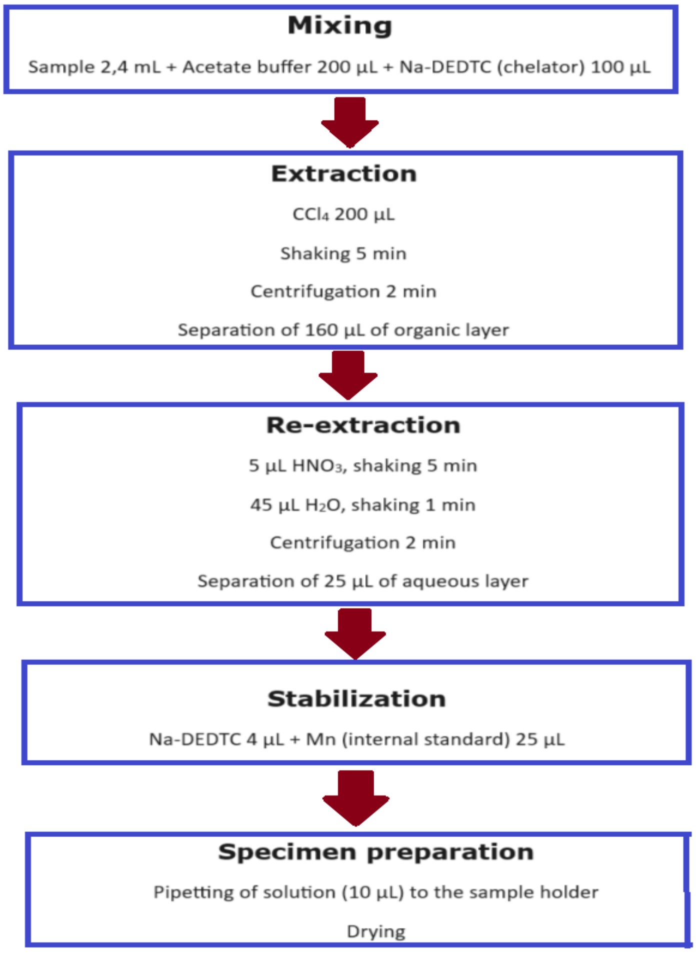


Fig. 1. Scheme of sample preparation

2.5. Determination of metal concentrations.

The TXRF spectra were registered using a Mo Kα (17.5 keV) X-ray source, working at 50 kV and 600 μA with an acquisition time of 1200s. Then, the resulting spectrum was automatically processed with the spectrometer software (Spectra 7, Bruker) using the Profile Bayes (regular fit) deconvolution mode. Element concentrations in the prepared sample were calculated using the internal standard method. The blank sample analysis result was subtracted from the obtained value. We calculated the metal concentrations in the initial sample according to the calibration and the dependence of the metal concentration in the re-extraction on its measured concentration in the initial solution. Twelve solutions of metals with different concentrations were used to carry out the calibration. We added NaCl to the calibration solutions to model the composition of seawater; its final concentration was 35 g L^{-1}. Using the Grubbs criterion [25], we excluded anomalous results from the obtained data and calculated the average value.

3. Results and discussion

3.1. Mercury stabilization in solution

We used extraction of heavy metal complexes with organic solvents to separate them from seawater with subsequent determination by various methods. Mercury, along with other heavy metals, can react with dithiocarbamates. We used sodium diethyldithiocarbamate (Na-DEDTC) as a complexing agent. Determining metals by the TXRF method directly in the extract is difficult because of the uneven distribution of the sample on the sample holder and the necessity to inject the internal standard into the organic phase. These difficulties can be eliminated by including the stage of re-extraction - the destruction of complexes under the action of acid and the transfer of metals into the aqueous layer. However, during back-extraction, mercury passes into a mobile form and can be lost while the sample is drying on the sample holder. Thus, stabilization of mercury compounds in the re-extraction is required, so we used a repeated addition of a complexing agent for this purpose. The method of drying the aliquot of the sample pipetted to the sample holder may also affect the result of the mercury determination. Drying can occur in a vacuum desiccator or on a temperature-controlled heating surface. We used 65 °C. We experimentally determined the sample drying method and the required volume of Na-DEDTC for subsequent analysis. For this purpose, we analyzed a standard mercury solution with a 500 μg L^{-1} concentration. The concentration of added Na-DEDTC varied from 0.03 to 0.10 %. The results are presented in Table 1. Without using Na-DEDTC, regardless of the drying method, we observed an almost complete loss of mercury, which was unacceptable during the analysis. The table shows that the best results are obtained if sodium diethyldithiocarbamate with a concentration of 0.07 % is used, regardless of the drying method. The measured mercury concentration during drying in a vacuum desiccator is slightly lower than when the sample holder is heated to 65 ° C due to the more extended contact of the sample with acid during vacuum drying (20 min and 5 min, respectively). Thus, we have proposed the original approach to eliminating the problem of mercury losses. For this purpose, sodium diethyldithiocarbamate must be added to the re-extract after the destruction of the complexes with nitric acid to hold mercury in the sample.

Table 1. Measured concentrations of mercury ions depending on the drying method and stabilizer (Na-DEDTC) concentration

Na-DEDTC concentration	Vacuum drying		Drying at 65°C	
	Concentration (μg L^{-1})	Recovery (%)	Concentration (μg L^{-1})	Recovery (%)
0	13	2.6	15	3.0
0.03	339	67.8	464	92.8
0.05	361	72.2	458	91.6
0.07	413	82.6	488	97.6
0.10	389	77.8	489	97.8

3.2. The pH effect on the extraction of the metal

The pH of the solution affects the completeness of elements bonding into chelate complexes and has its optimal value for each metal. In the case of group separation of metals, the best pH will be the one that allows extracting the most significant number of elements. We treated a standard solution containing 13 elements using buffer solutions with a pH in the range of 3.2 to 6.3 at the first stage. Metal concentrations in re-extract were determined in reference to the gallium standard solution and added at the last analysis stage. We did not take into account the content of elements in the blank sample in this experiment. Table 2 and Figure 2 show the results of two independent measurements for each pH value. According to the presented data, we can conclude that in the studied pH range, the concentration in the re-extract, in comparison with the initial solution, increases for all studied elements except manganese and arsenic. At the same time, the degree of extraction of various metals at fixed pH is different and is always significantly lower than 100%. Non-quantitative extraction of elements from the sample leads to the necessity of determining the concentration of each element according to the calibration. Our task was determining the pH that would provide the most complete extraction of mercury ions from the solution. Figure 2 shows the dependence of mercury concentration in the re-extraction on the pH. Mercury ions are most effectively extracted from the standard solution at a pH equal to 5.0. At pH = 5.0, in addition to mercury, other elements such as V, Cr (VI), Fe, Co, Ni, Cu, Zn, Se, Cd, Pb, and Bi were effectively concentrated.

Table 2. Element concentrations (µg L^{-1}) in re-extract at different pH of the buffer solution

pH	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	As	Cd	Hg	Pb	Bi
6.3	283	98	40	365	281	299	258	567	10.4	304	49	378	297
	294	97	38	366	287	304	268	581	7.7	296	54	381	306
5.9	432	131	27	521	425	446	393	763	8.7	465	84	579	472
	431	139	28	527	435	448	393	766	6.1	445	108	585	469
5.4	386	128	8.4	518	414	438	384	772	11.8	308	178	557	471
	390	137	9.5	541	428	441	387	776	12.1	363	126	567	466
5.0	500	167	3.5	766	627	683	571	1116	15.9	608	181	832	644
	481	168	4.0	760	612	672	552	1091	12.5	572	136	795	626
4.8	378	159	2.3	735	623	673	515	943	5.5	477	170	865	629
	376	154	4.7	741	614	671	511	931	7.2	453	135	854	624
4.4	309	176	0.0	750	620	678	566	676	6.9	763	158	939	636
	338	135	6.6	823	652	717	601	719	3.3	659	141	1011	681
4.3	198	158	0.0	651	497	578	463	361	7.3	710	91	929	515
	212	159	0.0	657	511	592	481	382	6.9	645	104	973	551
4.0	99	106	0.0	451	364	466	367	62	6.7	200	66	758	351
	92	104	0.0	443	361	454	356	59	7.4	254	67	753	356
3.6	83	65	1.9	373	237	317	248	30	7.1	24	42	848	274
	76	64	2.0	374	229	309	242	27	5.6	22	39	833	270
3.2	77	56	2.5	118	274	358	547	49	3.5	0.0	124	3.4	707
	70	59	2.5	133	281	371	559	50	3.0	0.0	150	4.0	730

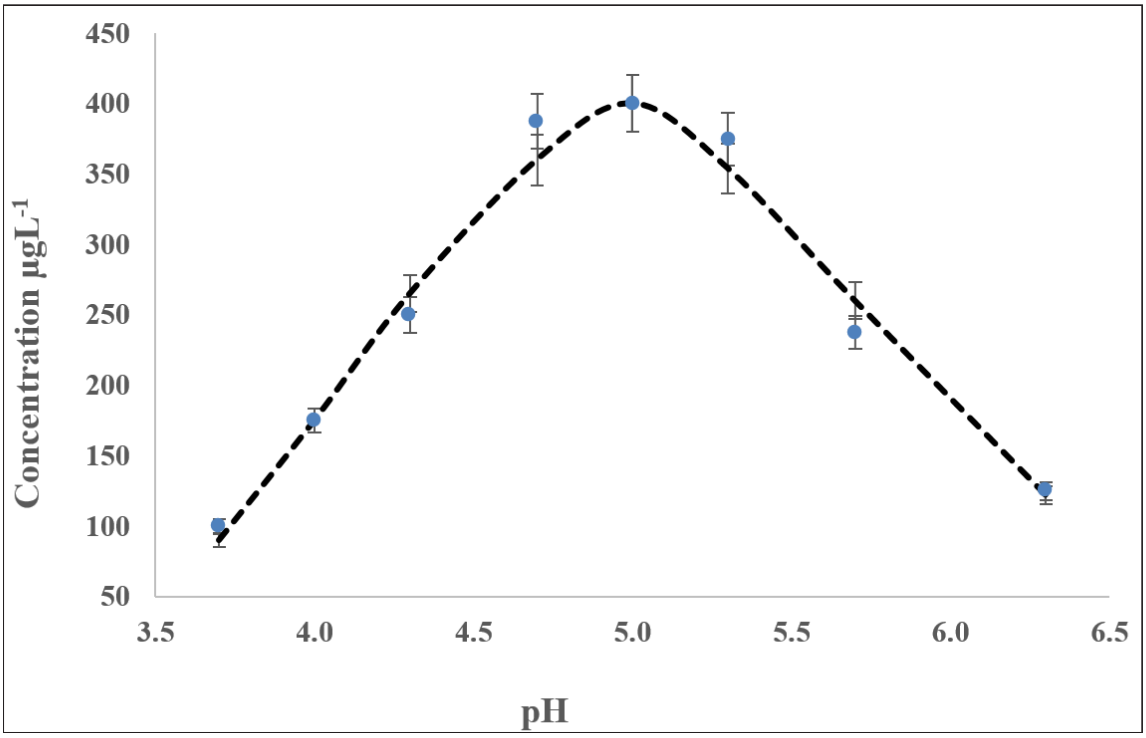


Fig. 2. Dependence of mercury concentration on the pH of buffer solution.

3.3. Calibrations obtaining

We obtained calibrations for 12 different elements, taking into account the influence of seawater's salt matrix. Given the low concentrations of elements in seawater, calibration data is necessary to determine accurately their concentrations. The concentrations are low because the object of study is seawater from the Arctic region, which is little subject to anthropogenic influence. We analyzed multi-element standard solutions with various concentrations to obtain calibrations for each metal. The concentration range was from 1 to 400 µg L^{-1} for mercury and approximately 2 to 1000 µg L^{-1} for lead, and other elements [26]. While performing the analysis, we used previously selected pH and stabilizer concentration (Na-DEDTC). We performed six parallel measurements for each calibration solution per the abovementioned procedure. We used 12 multi-element calibration solutions; 8 of them had approximately equal concentrations of all elements, covering the entire range of concentrations under study. In addition, for each element, we used two solutions with low concentration (10 µg L^{-1}) at the average concentration of the remaining elements (100 µg L^{-1}) and two solutions with high concentration (1000 µg L^{-1}) at the average concentration of the remaining elements (100 µg L^{-1}). We chose the lowest value based on the possibility of directly determining the concentration of these elements using a spectrometer. The solubility of chelate complexes in tetrachloromethane limits the maximum concentration. We previously measured the exact concentration of calibration solutions obtained by mixing mono-element standards (State standard reference samples of metals) in reference to the standard gallium solution. Figure 3 represents the example of the X-ray fluorescence spectrum of one of the standard solutions. We considered the calibrations obtained for all elements as linear, described by the equation $y=ax+b$. Parameter a is the enrichment factor. The deviation of parameter b from zero observed for some elements is explained by calibration inaccuracy. We also calculated the correlation coefficient R^2, and its values are more than 0.8, indicating the obtained equations' correctness (Table 3). Table 3 also shows the maximum permissible concentrations for the elements under study [27]. The lower detection limit was calculated based on the standard deviation of the background signal under the element line, according to Equation 1.

$$LOD_i = \frac{3 \cdot \sigma_{Bg\,i}^{rel} \cdot C_{IS}}{S_{IS}^{rel} \cdot K_i}$$

(Eq.1)

LOD_i: lower limit of detection of element *i*, µg L^{-1}

$\sigma_{Bg\,i}^{rel}$: The standard deviation of the relative background intensity under the analytical line of element *i*.

C_{IS} : Internal standard concentration (500 µg L-1 Mn).

S_{IS}^{rel} : The sensitivity coefficient of element *i* is normalized by the sensitivity coefficient of the internal standard.

K_i : Enrichment factor of element *i*.

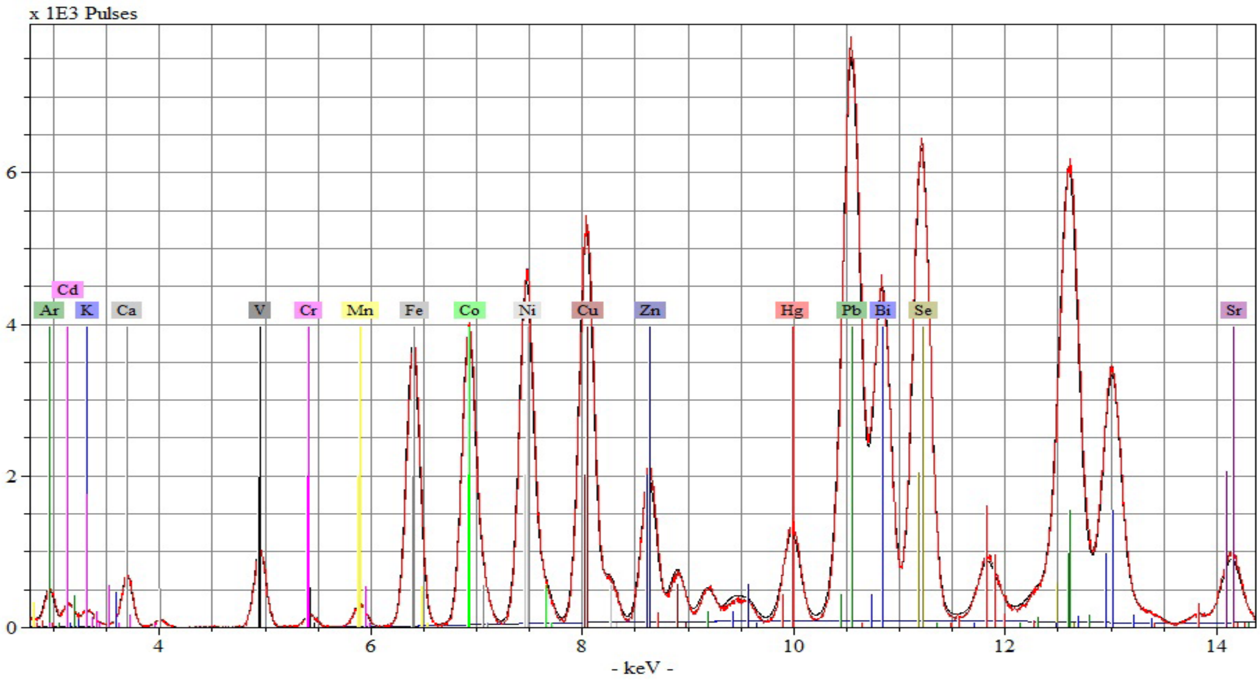


Fig. 3. X-ray fluorescence spectrum of the standard solution with a concentration of 500 µg L^{-1}; internal standards: 500 µg L^{-1} Mn and 500 µg L^{-1} Sr.

Table 3. The concentration range and parameters of calibrations of elements are determined

Element	**Conc. range (µg L^{-1})**	**a**	**b**	**R^2**	**LOD (µg L^{-1})**	**MPC (µg L^{-1})**
V	2.0-1000	5.25	0.16	0.89	1.0	1
Cr (VI)	1.5-1100	14.12	-0.99	0.99	0.1	20
Fe	15.0-1100	10.42	1.24	0.83	0.7	50
Co	2.0-1050	10.13	0.77	0.85	0.6	5
Ni	2.0-1100	10.57	0.54	0.81	0.4	10
Cu	2.0-1000	12.67	0.21	0.84	0.3	5
Zn	1.5-1100	25.10	-4.87	0.96	0.1	50
Se	1.5-1100	4.27	-2.89	0.99	0.6	1.6
Cd	1.5-1050	18.53	0.50	0.99	7.0	10
Hg	1.0-400	11.81	0.94	0.80	0.1	0.1
Pb	2.5-1200	19.68	1.12	0.93	0.1	10
Bi	2.0-1000	10.77	-0.50	0.86	0.3	100

a: Slope of linear calibration (observed enrichment factor);
b: Intercept of linear calibration;
MPC: Maximum permissible concentration of the element

Figures 4a (for Pb, Zn, Cd, Cr), 4b (for V, Fe, Co, Se), and 4c (for Ni, Cu, Hg, Bi) show the calibration for all elements and lead. Table 3 represents the parameters of metal calibrations. The technique was validated using the "add-found" method. The seawater sample was analyzed, mixed with a standard metal solution, and analyzed again. The obtained results are shown in Table 4.

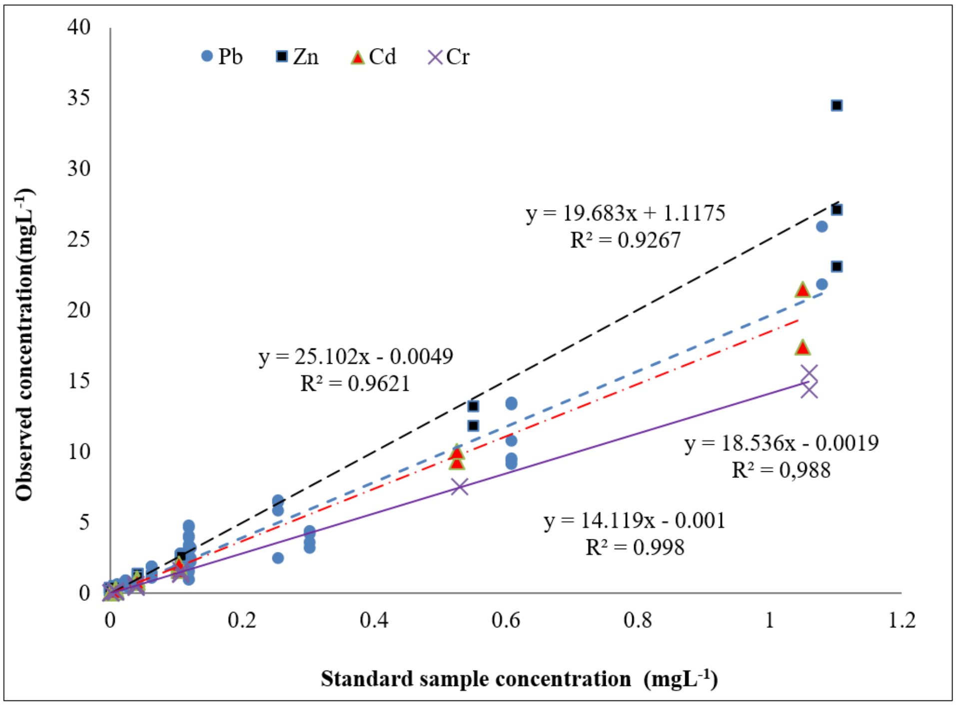


Fig. 4a. Calibration for different elements (Pb, Zn, Cd, Cr)

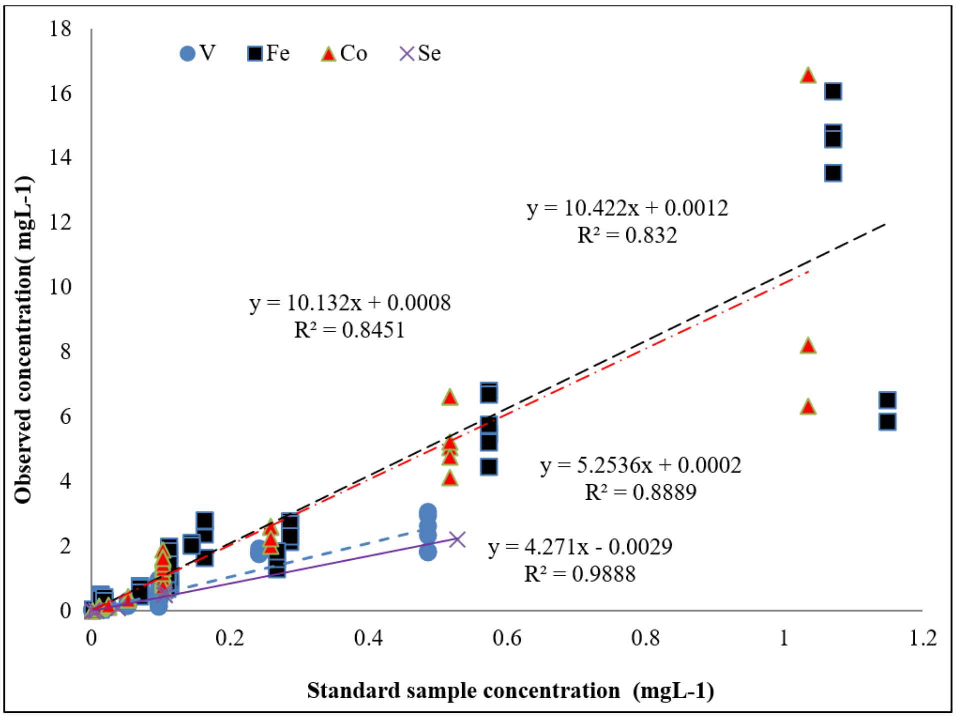


Fig. 4b. Calibration for different elements (V, Fe, Co, Se)

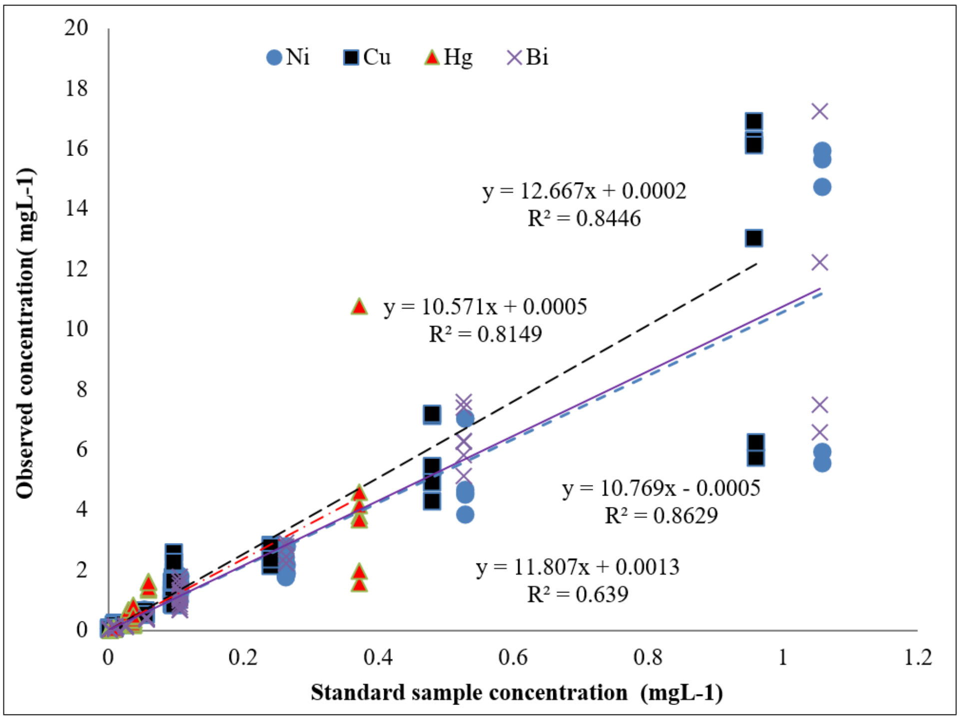


Fig. 4c. Calibration for different elements (Ni, Cu, Hg, Bi)

Table 4. Results of method validation for metal determination by procedure

Element	Add Standard ($\mu g\ L^{-1}$)	Found sample ($\mu g\ L^{-1}$)	Found standard ($\mu g\ L^{-1}$)	Recovery (%)
V	----	4.60	----	----
	2.50	6.71	2.11	85
Cr (VI)	----	0.11	----	----
	0.20	0.32	0.22	105
Fe	----	8.2	----	----
	20.0	29.0	20.8	104
Co	----	----	----	----
Ni	----	2.82	----	----
	5.0	7.22	4.4	88
Cu	----	33.4	----	----
	100.0	129.4	95.9	96
Zn	----	29.8	----	----
	100.0	115.8	86.0	86
Se	----	----	----	----
Cd	----	----	----	----
Hg	----	----	----	----
Pb	----	4.99	----	----
	10.0	14.50	48.1	95
Bi	----	----	----	----

3.4. Investigation of the content of elements in samples of seawater of the Arctic region

We used this approach to determine the element's content in Arctic seawater. For this purpose, 39 samples of seawater were obtained during the expedition work on the research vessel "Academik Mstislav Keldysh" AMK-86 in 2020 as part of an international marine expedition. The International Siberian Shelf Study (ISSS) Program is a Russian-Swedish-led international collaboration. Seawater samples were taken in different seas with different salinity and trace element content. The obtained results are presented in Table 5.

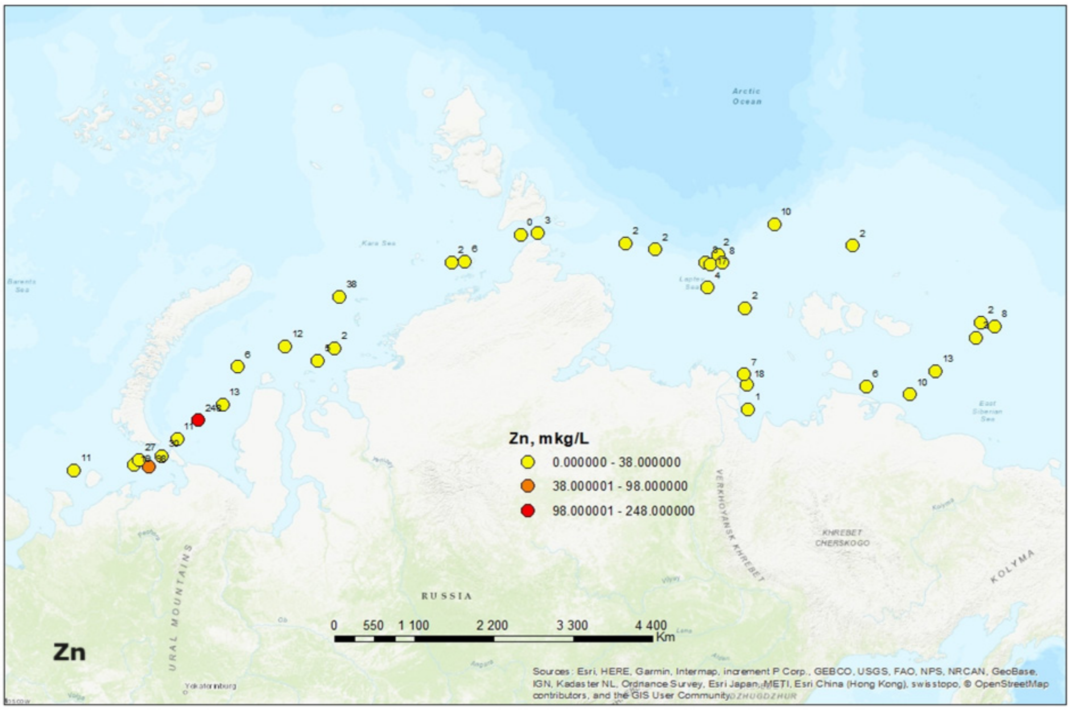
Table 5. The results of the determination of elements in the seawater of the Arctic region*

C (μg L^{-1})	V	Cr (VI)	Fe	Ni	Cu	Zn	Pb
Sw20_1	3.86	----	5.80	3.88	18.04	11.42	1.33
Sw20_2	4.42	----	17.91	5.42	13.33	18.79	1.62
Sw20_3	4.09	----	17.50	13.55	208.11	98.13	8.77
Sw20_4	4.60	0.11	8.20	2.82	33.44	29.81	4.99
Sw20_5	2.28	----	65.50	9.37	55.08	247.72	67.86
Sw20_6	1.96	0.58	13.11	2.09	11.88	11.71	0.64
Sw20_7	3.16	----	11.52	3.57	43.00	38.50	3.34
Sw20_8	2.74	----	37.22	1.43	3.97	5.60	0.39
Sw20_9	1.83	0.31	41.81	1.10	1.84	3.36	0.28
Sw20_10	3.34	0.19	4.80	0.59	0.69	1.85	1.36
Sw20_11	3.64	0.03	5.40	0.69	0.84	8.41	0.33
Sw20_12	3.39	0.24	10.00	1.38	2.37	16.81	0.92
Sw20_13	2.17	0.30	15.40	0.77	1.61	2.13	0.17
Sw20_14	2.43	0.11	7.30	1.29	0.93	7.97	0.26
Sw20_15	2.34	-	29.40	0.62	1.57	9.71	0.33
Sw20_16	2.07	0.21	8.00	0.85	0.94	2.31	0.55
Sw20_17	2.25	----	19.80	1.31	1.25	2.00	0.09
Sw20_18	1.92	----	7.40	1.15	2.26	7.99	0.55
Sw20_19	1.73	0.12	22.20	1.01	1.08	2.91	0.39
Sw20_20	1.54	----	92.20	1.05	0.77	13.46	0.09
Sw20_21	3.02	1.17	709.50	1.99	3.96	10.38	0.38
Sw20_22	1.04	0.38	298.30	1.11	1.40	5.63	0.17
Sw20_23	1.15	0.17	7.60	1.30	2.72	1.18	0.21
Sw20_24	0.26	0.10	131.80	0.55	3.41	17.57	0.20
Sw20_25	1.00	----	45.60	1.05	1.13	6.54	----
Sw20_26	2.36	0.13	11.90	1.36	1.03	2.36	0.20
Sw20_27	2.33	0.57	239.10	1.34	1.50	3.56	0.31
Sw20_28	2.95	0.16	64.80	0.65	1.16	1.77	0.61
Sw20_29	2.62	0.40	32.20	1.31	1.30	0.33	----
Sw20_30	1.75	----	31.10	1.27	0.89	1.70	0.17
Sw20_31	1.31	----	88.00	0.84	1.20	2.22	0.04
Sw20_32	2.32	0.23	123.70	0.95	1.13	5.12	----
Sw20_33	3.74	0.40	27.90	0.83	1.19	6.50	0.26
Sw20_34	3.02	0.41	----	1.37	1.46	13.39	0.18
Sw20_35	3.02	0.09	53.30	0.78	0.72	10.51	----
Sw20_36	5.09	0.04	0.20	0.37	1.80	27.02	0.14
Sw20_37	4.19	0.34	28.90	0.37	1.43	4.20	0.14
Sw20_38	2.52	0.10	36.20	0.58	2.21	10.00	0.35
Sw20_39	1.79	----	61.00	0.47	0.65	3.27	0.29

\- below the limit of quantitative detection

*Co, Se, Cd, Hg, and Bi not detected

The approach allowed us to determine the content of the following elements: V, Cr(VI), Fe, Ni, Cu, Zn, Pb, Co, Se, Cd, Hg, Bi. The advantage of the proposed approach is the simultaneous determination of 12 elements, including mercury, with a simple separation procedure to eliminate the interfering influence of the salt matrix. During the study, we used the previously established parameters of sample preparation and determination of elements by calibrations. We used a blank sample (deionized water that has passed all stages of sample preparation, including acidification) to consider the presence of element impurities in the used reagents. In addition to determining trace elements in the samples, we determined the dissolved oxygen and pH of the seawater at the moment of sampling in the vast majority of cases. The Data visualization is in Figure 5. Based on the data visualization, we can conclude that the content of the studied elements in seawater is low, and most are below the detection limit. We have revealed no dependence of the element's concentration in seawater on currents or river runoff. The average concentrations (µg L^{-1}) for V, Cr (VI), Fe, Ni, Cu, Zn, and Pb are 40.0, 2.87, 843, 13.6, 18.8, 98.5, and 2.64, respectively. However, the average concentration value is not used correctly because of the abnormally high values of metals at specific points. It is more accurate to use the median values of concentrations, which were 2.39, 0.21, 28.9, 1.11, 1.46, 6.54, 0.33 µg L^{-1} for V, Cr (VI), Fe, Ni, Cu, Zn, Pb, respectively. We also conducted a correlation analysis (Table 6) of the element content. We observed correlations for pairs of elements: Cr—Fe, Ni—Cu; Ni—Zn; Ni—Pb; Zn—Cu; Zn—Pb; Pb—Cu. We also found the correlation between dissolved oxygen and pH, as well as correlations between V—pb and Ni—O_2. The concentration of vanadium does not correlate with the concentrations of other found elements. Iron correlates only with chromium and with no other elements. Similarly, chromium correlates only with iron. The content of copper, zinc, nickel, and lead correlates with each other. Thus, vanadium, iron, and the group (Cu, Ni, Zn, Pb) come from different sources. A group of elements (Cu, Ni, Zn, Pb) have similar geochemical characteristics and probably come from the same source. The presented methodology allows us to estimate the levels of seawater pollution in reference to environmental standards. The study found that the concentrations of trace elements in seawater are below the MPC.



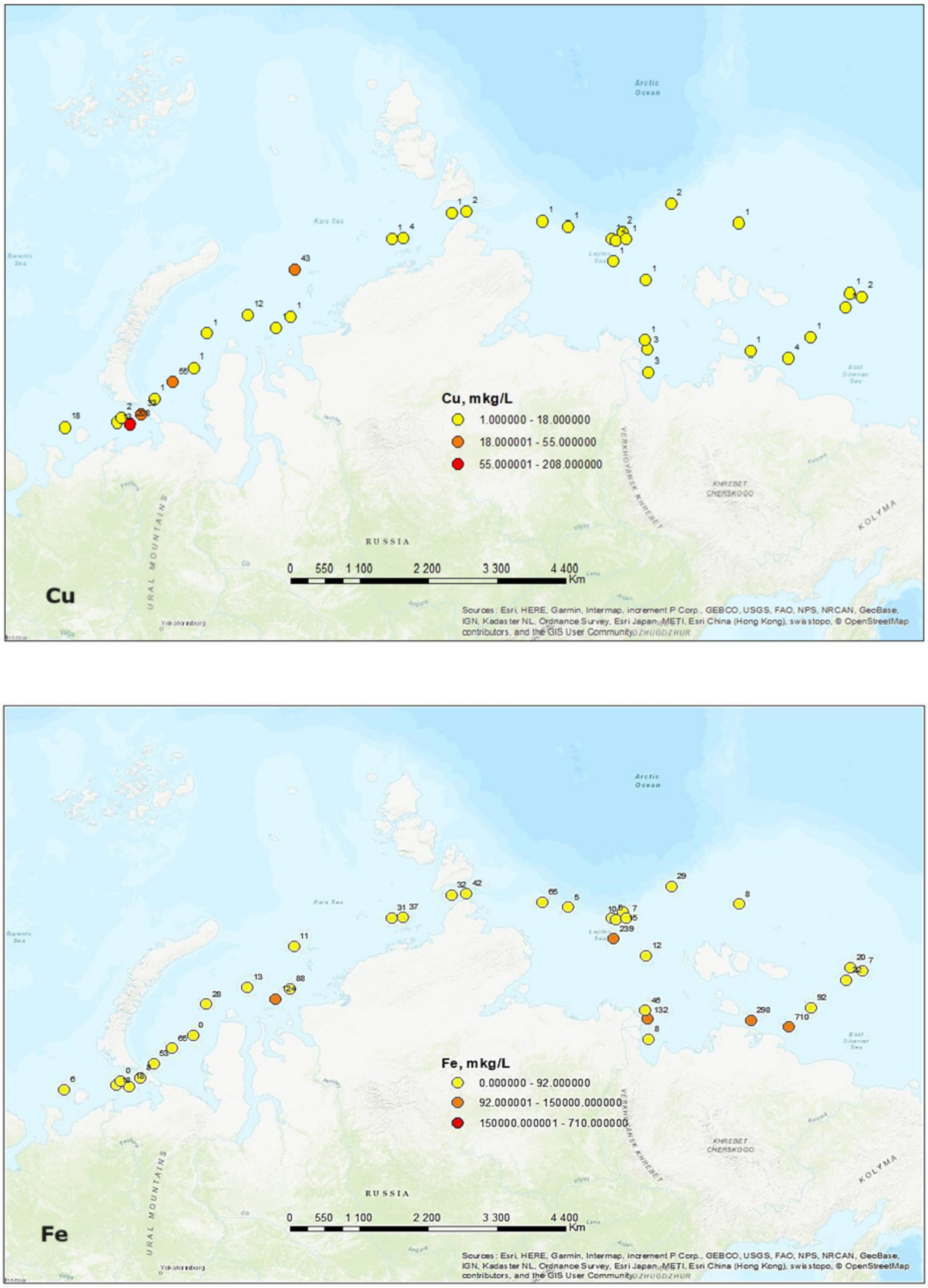


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Fig. 5. The distribution of Fe, Cu, and Zn in the seawater of the Arctic seas

Table 6. Pearson correlations between elements, dissolved oxygen, and pH

	V	Cr	Fe	Ni	Cu	Zn	Pb	pH	O_2
V	1								
Cr	0.061	1							
Fe	0.028	0.772^{**}	1						
Ni	0.393^{*}	0.152	0.033	1					
Cu	0.415^{*}	0.173	0.083	0.931^{**}	1				
Zn	0.150	0.180	0.014	0.781^{**}	0.553^{**}	1			
Pb	0.065	0.151	0.013	0.612^{**}	0.328	0.963^{**}	1		
pH	0.639^{**}	0.202	0.291	0.367	0.288	0.255	0.219	1	
O_2	0.354	0.013	0.035	0.565^{**}	0.458^{*}	0.417^{*}	0.355	0.635^{**}	1

*. The correlation is significant at the 0.05 level (two-tailed).

4. Conclusion

We found that during sample preparation for mercury bonding in seawater, an additive of sodium diethyldithiocarbamate with a concentration of 0.07 % is required after re-extraction. The optimal pH for the most complete extraction of mercury ions is equal to 5. We also obtained individual calibrations for 12 trace elements. Concentration ranges and lower limits of detection have been determined. We have determined the concentrations of elements in the seawater of the Arctic Seas and calculated the median values of concentrations. The presented methodology allows us to estimate the levels of seawater pollution in reference to environmental standards. The study found that the concentrations of trace elements in seawater are below the MPC. We found correlations between the content of certain elements, pH, and dissolved oxygen content.

5. Acknowledgements

This research was performed using instrumentation at the Core Facility Center “Arktika” of the Northern (Arctic) Federal University. It was supported by the Ministry of Science and Higher Education of the Russian Federation (state assignment project No. FSRU-2024-0003). The authors have no relevant financial or non-financial interests to disclose.

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