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Water-soluble polymers for spectrophotometric and flow injection determination of cobalt with nitroso-R-salt

T.G. Dzherayan ^{a,*}, V.M. Shkinev ^a, L.K. Shpigun ^b, P.M. Kamilova ^b,
K.E. Geckeler ^c

^a Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, 117975 Moscow, Russia

^b Institute of General & Inorganic Chemistry, Russian Academy of Sciences, Leninsky Prospect 31, 117907 Moscow, Russia

^c Laboratory of Applied Macromolecular Chemistry, Department of Materials Science and Engineering,
Kwangju Institute of Science and Technology, 1 Oryong-dong, Buk-gu, Kwangju 500 712, South Korea

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Dedicated to Professor Dr Boris Ya Spivakov, Vernadsky Institute of Geochemistry and Analytical Chemistry, Russian Academy of Sciences, on the occasion of his 60th birthday.

Abstract

The water-soluble polymers poly(ethylenimine), quaternized poly(ethylenimine), and poly-4-vinyl(*N*-benzyltrimethyl) ammonium chloride were found to be able to change the kinetics of the reaction of cobalt with nitroso-R-salt and the optical density of the cobalt complex formed. The optimum pH range for the complex formation was a wide range from 1 to 10 and at pH 2 the reaction developed instantly. The calibration graph was linear in the range $0.005\text{--}2\text{ }\mu\text{g ml}^{-1}$. The effective molar absorptivity coefficient of the complex was equal to $(2.8 \pm 0.08)10^3$. A spectrophotometric determination method for cobalt with nitroso-R-salt in the presence of water-soluble polymers (before and after membrane preconcentration) and a colorimetric flow injection method were developed. For the flow injection-based spectrophotometric determination, the calibration graph was linear in the concentration range of $0\text{--}4.0\text{ }\mu\text{g ml}^{-1}$ cobalt with a regression coefficient of 0.9992. The relative standard deviation (R.S.D.) for the determination of $1.0\text{ }\mu\text{g ml}^{-1}$ cobalt was 0.9% (ten replicate injections), and at all concentration measured, the R.S.D. of the data was below 5.0%. The proposed FI procedure was applied to river water samples after membrane preconcentration of cobalt. The limit of detection was 4 ng ml^{-1} . © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Determination of cobalt; Water-soluble polymers; Spectrophotometry; Flow injection

1. Introduction

It has been shown that organic microheterogeneous systems (micellae, zoles, emulsions) can be successfully used in analytical chemistry for devel-

* Corresponding author. Tel.: +7-95-939-7001; fax: +7-95-938-2054.

E-mail address: dzherajan@mail.ru (T.G. Dzherayan).

oping new methods of determination or improving previously established methods and in particular to improve the conditions of metal complexation with organic reagents (OR) [1–3].

The addition of surfactants is one way for microheterogeneous systems formation. Generally, it results in increasing of the reaction speed. This effect could be explained by the concentration of the OR or the metal ion at the micelle surface or its nucleus. Sometimes the micellar phase pH differs from the pH of the bulk phase. It is possible that the reaction centers of the analytical OR responsible for the reaction could be situated in microphase. However, such approaches suffer from several practical disadvantages including small concentration ranges and a defined ratio of components for the micellar phase formation, when surfactants are used.

A similar effect of complexing in micellae can be achieved by using water-soluble polymers (WP). The main advantage of this approach is a wider range of suitable WP concentration and pH values that is why a very broad range of possibilities to improve the analytical color reaction characteristics can be achieved. For example, simultaneous kinetic determination of nickel(II) and cobalt(II), based on the complex formation reaction between these ions and 5-octyloxymethyl-8-quinolinol in the non-ionic micellar medium provided by Triton X-100, has been proposed [3]. Such systems could be also applied for element concentration with the help of membranes [4–9]. Micellar media can also enhance the sensitivity and selectivity for the determination of ions [3,5]. Our experience in this area indicates that the main analytical characteristics of the Cu and 4-(2-pyridylazo)resorcinol color reaction can be improved by the use of WP [6].

The aim of this paper is to study the interaction of nitroso-R-salt (NRS) with Co in presence of WP, its kinetic role for spectrophotometric and flow injection methods, the possibility of cobalt membrane concentration and to develop methods of spectrophotometric and flow injection determination of cobalt in waters.

2. Experimental

2.1. Reagents and solutions

All chemicals were of analytical reagent-grade. Glass-distilled water was used throughout.

A stock standard solution of Co(II) (1.2×10^{-4} M) was prepared by dissolving CoCl_2 . The stock solution was further diluted with 0.01 M HCl. A 0.01 M solution of nitroso-R-salt (NRS) was prepared by dissolving an exactly weighed sample of the reagent from Chemapol (Hungary). Introducing 0.1 and 1.0 M HCl or NaOH adjusted the necessary pH value. A 50% solution of poly(ethylenimine) (PEI) [6] from BASF (Germany), a 10% solution of quaternized poly(ethylenimine) (QPEI) [7,8], synthesized at the University of Tuebingen (Germany), and a poly-4-vinyl-(*N*-benzyltrimethyl) ammonium chloride (VA-2), synthesized at the BIOLAR plant (Olaine), were used as the water-soluble polymers (WP). The WP were washed with 10 volumes of distilled water in the filtration cell prior to use with the same membranes that were used for the experiment, to free them from the monomeric impurities.

2.2. Apparatus

The absorbance at 500 and 550 nm was measured on a Specord UV–VIS spectrophotometer. The pH of the solutions was adjusted by the addition of HCl or NaOH and checked with the pH-meter. Membrane filtration was conducted on a UFM-03-type instrument [6]. Membranes of the UMP-P type (produced by Tasma) and filters ‘nuclear’, pore size 0.07 μm , were used.

All FI experiments were performed by using ‘FIASStar-5020’ equipment (Tecator). The 5020 identifies the rise of absorbance as a peak and defines a baseline value. The absorption spectra (400–700 nm) as well as other spectrophotometric measurements were recorded on ‘FIASStar-5023’ spectrophotometer consists of the 5032 Detector Controller and the 5023-011 optical unit with 1-cm flow cell. The integration time was changed within the range 0.01–0.1 s.

2.3. Procedure

A series of solutions of the WP and NRS were prepared in 5.0 ml volumetric test tubes, 2.0 ml of distilled water and the defined volumes of cobalt chloride solution were added, the required pH was adjusted by introducing HCl and NaOH, the mixtures were diluted to 4.0 ml with distilled water, mixed thoroughly, and the optical density of solution obtained was measured relative to the solution of the control experiment or relative to distilled water in a 1-cm cuvette. The calibration curve for the spectrometric determination of 0.01–2.0 mg ml⁻¹ cobalt was conducted according to the procedure given at pH 2 with 2.65×10^{-4} M NRS and 0.25% VA-2.

To select the optimum system of cobalt retention we used the experimental procedure described above and varied the concentrations and ratios of the components in the reaction mixtures. The obtained solutions were diluted with water to 40–200 ml, and the necessary pH value was adjusted. The completeness of the retention of cobalt with the WP in the form of a complex with NRS was monitored by analyzing 4 ml fractions of the filtrate, collected during membrane filtration. The retention of cobalt in percent was calculated according to the formula $R = (C_{\text{init}} - C_f) / C_{\text{init}} \times 100\%$, where C_{init} is the initial cobalt concentration; C_f is the cobalt concentration in the filtrate samples [8]. To calculate the balance of the distribution of cobalt, its content in the concentrate was determined. In a number of cases, the cobalt-containing solution was introduced into the reservoir, and the solution of the mixture of WP and NRS was passed through the filtration cell with solution from the reservoir. The cobalt content was determined both in the filtrate and in the concentrate and the retention values were calculated from these data.

3. Results and discussion

3.1. Absorption spectra

NRS forms a red complex anion with cobalt

at pH 6 in different buffer solutions [10]. The absorption maximum of the colored compound centers at 415 nm, but the absorption was measured at 555 or 560 nm, respectively, because the reagent does not absorb in this range. The absorption spectra of the reagent and its complex with cobalt under optimum conditions for complex formation in the presence of WP (curves 1, 3) and in the absence (curves 1, 2) both at pH 2 and curve 4 in the absence of VA-2 at pH 6 are presented in Fig. 2. It is shown that the presence of WP did not influence the position of maxima of absorption spectrum of the reagent and its cobalt complex. However, the optical density of the cobalt complex with the NRS salt increases sharply. The absorption of the reagent itself in the region of absorption of the complex is negligible.

3.2. Influence of pH

NRS does not form a red complex at pH 1–2 under these conditions; however, there is an interaction at pH 6 in different buffer solutions. For example, by using an acetate buffer solution (pH 5) it needs the boiling temperature to produce such a complex. In order to increase the selectivity, the pH was changed to the acidic area and the influence of polymers with different functional groups on the color reaction of cobalt with NRS was studied. For example, the dependence of the optical density of the cobalt complex with NRS in the presence of VA-2 is shown in Fig. 3. This figure clearly illustrates that the optimum pH range for complex formation is a wide range of 1–10. It allows suggesting an anion-exchange mechanism for the interaction between the WP and NRS. Thus, quaternary nitrogen atoms link to dissociated, strong acid SO₃H groups of the reagent, that do not participate in the conjugation system and consequently do not influence the functional groups of the analytical reagent. Such a mechanism is confirmed by the fact that the presence of WP does not influence the position of maxima of absorption spectrum of the reagent and the complex.

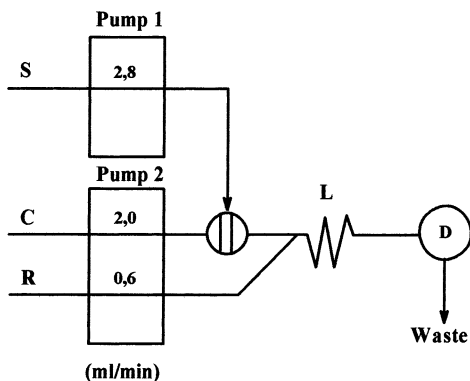


Fig. 1. Schematic diagram of the flow injection manifold used for determining cobalt: C, carrier; R, reagent; S, sample; L, reaction coil; D, detector.

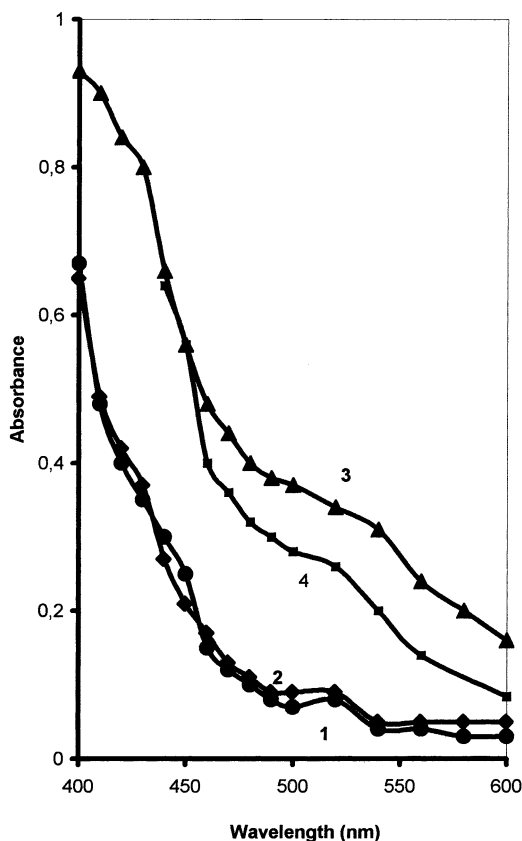


Fig. 2. Absorption spectra of solutions of NRS in the absence (1) and in the presence (1) of VA-2 [the same curves] and its complex with Co in the absence (2) and in the presence (3) of VA-2 at pH 2 (2, 3) and in the absence of VA-2 at pH 6 (4). $C_{Co} = 1.7 \times 10^{-5} \text{ mol dm}^{-3}$, $C_{NRS} = 2.65 \times 10^{-3} \text{ mol dm}^{-3}$, $l = 10 \text{ mm}$.

3.3. Influence of water-soluble polymer nature and concentration

To optimize the spectrophotometric determination, the influence of polymers with several functional groups on the color reaction of cobalt with NRS was studied in conjunction with membrane filtration. The polymers contained primary, secondary, and tertiary nitrogen atoms (PEI), in addition quaternary nitrogen atoms (QPEI), and solely quaternary nitrogen atoms (VA-2). The system Co(II)–NRS–VA-2 was studied in more detail. The dependence of the optical density of the complex on the content of VA-2 in the reaction mixture is shown in Fig. 4. As it can be seen, three parts of the curve can be discerned: when the VA-2 content increases from 0 to $5 \times 10^{-4}\%$, the optical density of the complex also increases gradually (part I). This may be attributed to the partly dehydration of the cobalt ion and to partly decomposition of NRS due to ion exchange association of positively charge polymer with ligand anionic sulfo-group and facilitate Co–NRS complex formation. Then, at VA-2 concentrations of 5×10^{-4} –0.25%, one can observe a solubility decrease of the complex and reagent (part II). That may be traced back to the aggregation of NRS molecules, when SO_3H -groups of the reagent are close to polymer molecules with quaternary nitrogen atoms and hydrophobic polyvinyl moieties. Finally, when the VA-2 content is higher than 0.25%, agglomeration occurs in an polymer excess (part III). An analogous mechanism was suggested in [6]. Optimum VA-2 concentrations are in the range between 0.25 and 2% (Fig. 4). At VA-2 concentrations $> 2\%$, the solutions became very viscous.

3.4. Influence of reaction time

The reaction of cobalt with NRS in the absence of WP practically did not proceed at room temperature at pH 2. In contrast, when any WP (PEI, QPEI, and VA-2) is added to the solution, the reaction developed instantly. However, at pH 1, the time needed to develop the optical density was

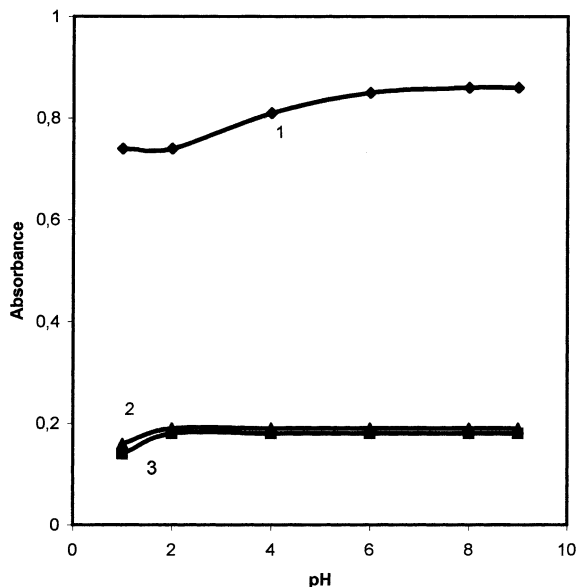


Fig. 3. Optical density of the complex of Co with NRS in the presence (1) of 2% (w/w) VA-2 and in its absence (2), and optical density of NRS in the presence (3) and in the absence (3) of VA-2 [the same curves], as a function of the pH. $C_{Co} = 1.7 \times 10^{-5}$ M, $C_{NRS} = 2.65 \times 10^{-3}$ M, $\lambda = 500$ nm. $L = 20$ mm.

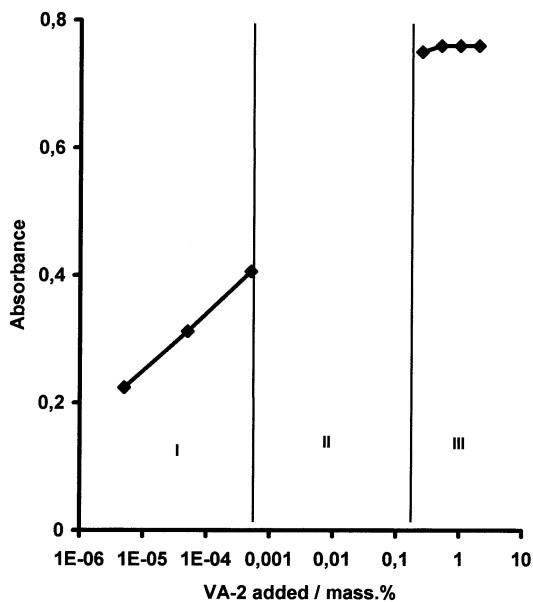


Fig. 4. Optical density of the complex of Co with NRS as a function of VA-2 concentration% (w/w) at pH 2. $C_{Co} = 1.7 \times 10^{-5}$ M; $C_{NRS} = 2.65 \times 10^{-3}$ M, $\lambda = 500$ nm, $l = 20$ mm.

longer, compared with experiments carried out at pH 2–6.

3.5. Analytical characteristics and composition of the complexes

The relationship between the optical density and the cobalt concentration at a NRS concentration of 2.65×10^{-4} M and at a VA-2 concentration of 0.25% ($l = 10$ mm) is linear in the range $0.005\text{--}2 \mu\text{g ml}^{-1}$. Using a higher NRS concentration could extend linearity of the plot. The effective molar absorptivity coefficient of the complex is equal to $(2.8 \pm 0.08)10^3$. The method of isomolar series and limiting saturation yielded the ratio Co:NRS = 1:6, while a value of Co:NRS = 1:3 was reported according to [10]. Thus, the number of ligands in the presence of WP is much higher and the increase of the molar absorption coefficient could be explained by this fact. An analogous effect was observed for surfactants [3].

3.6. Interferences

According to the data in [10], alkali, alkaline earth metals, chlorides, sulfates, nitrates, citrate ions in high concentrations, 10-multiple excesses of Fe(III), as well as Mn(II), Zn(II), Cd(II), Pb(II), and Sn(II), do not interfere with the cobalt NRS reaction. On the other hand, Cu(II) and Ni(II) reduce the values of cobalt determination. However, the procedure is very difficult and it is multistep process, including evaporation, boiling with acids, dissolution of precipitation followed by a sequence of boiling with HNO_3 , etc.

The absence of VA-2 allowed the development of the reaction at pH 2 and to increase the reaction selectivity with respect to the elements, which interfere with the reaction. To evaluate the selectivity, the concept of the selectivity factor was used in this work. That is based on the ratio of the amounts of an extraneous element (cation) and the element to be determined, limited to a range of optical density of the solutions not exceeding 5%. The influence of interfering compounds was analyzed relative to a solution of $1 \mu\text{g ml}^{-1}$ Co(II) at a reagent concentration of 2.65×10^{-4} M. This content corresponds to the middle

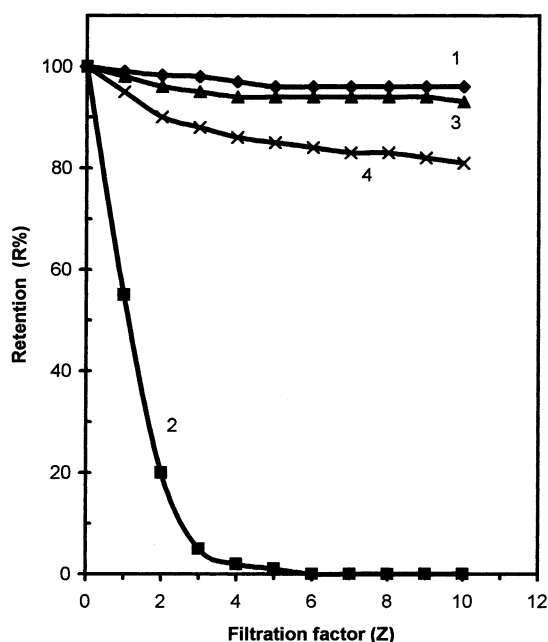


Fig. 5. Retention percent of Co (1,2) [alone] and Co in presence of 0.5 M Al (3) and Mn (4) by using of QPEI (1–4) and NRS (1, 3, 4) at pH 2 as a function of the filtration factor (Z).

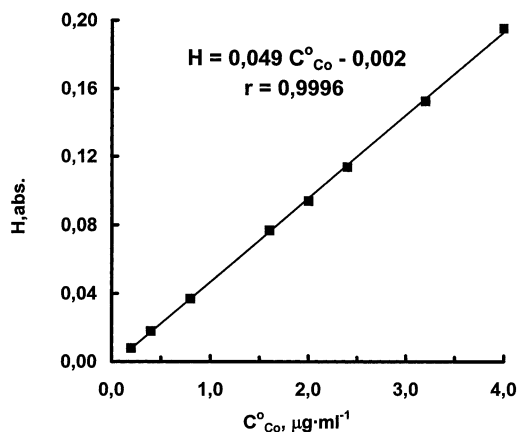


Fig. 6. The calibration graph and signals for the flow injection determination of cobalt.

part of the calibration curve, where the optical density of the solution in 1-cm cuvette is equal to 0.5.

The following multiple excesses (by mass) did not interfere with the determination of 1 µg

cobalt: 240 Al(III), Mn(II), Ni(II); 240 Fe(III) (in the presence of F⁻). At a reagent concentration of 3 M, even a 240-multiple excess of Cu did not interfere with the cobalt determination.

3.7. Effect of membrane filtration

Cobalt was concentrated by diafiltration, where a mixture of reagents of the optimum composition containing the test solution was introduced into a filtration cell and then the solution was filtered under pressure until the required volume of concentrate was obtained. Membrane filtration increases the selectivity for the determination of cobalt by removing the extraneous compounds. The results of cobalt retention *R* (a ratio of cobalt concentration in solution over the membrane and under the membrane) as a function of the ratio of filtrate volume to cell solution volume (*Z*) are shown in Fig. 5, where QPEI was used for retention.

The retention of cobalt with a WP was studied in the presence of NRS (curve 1) and in the absence (curve 2) (Fig. 5). As one can see, in the absence of the NRS salt, cobalt is not retained. This can be explained by the impossibility of an interaction of cobalt with WP in the absence of NRS. By using membrane filtration, a triple species Co–NRS–WP can be formed and retained over the membrane. The cobalt concentrations in the presence of 0.5 M Al(III) and Mn(II) are also shown by curves 3 and 4, in Fig. 5. Consequently, in the presence of WP, the analytical characteristics of the photometric reaction (sensitivity, selectivity, rate) of cobalt and NRS are improved and especially in conjunction with membrane filtration. Also absolute concentration and additional selectivity could be achieved.

4. FI spectrophotometric procedure and application

In order to make the determination of cobalt more rapid, more accurate and simpler, the complex formation of cobalt (II) with NRS in the presence of WP was utilized as indicator reaction in a FI method. On the basis of the studies on

Table 1

Results of the flow injection spectrophotometric determination of Co(II) in synthetic and real water samples

Sample	Concentration of Co(II) ($\mu\text{g ml}^{-1}$)		Recovery (%)
	Added	Found ($P = 0.95, n = 4$)	
Zn ($50 \mu\text{g ml}^{-1}$)	1.00	0.99 ± 0.02	99.0
Fe ($10 \mu\text{g ml}^{-1}$)	4.00	4.08 ± 0.09	102.0
Ni ($100 \mu\text{g ml}^{-1}$)	0.50	0.52 ± 0.02	104.0
	2.00	1.98 ± 0.06	99.0
Cu ($5 \mu\text{g ml}^{-1}$)	3.00	3.2 ± 0.2	106.7
	4.00	3.9 ± 0.3	97.5
River water	0.000	0.004 ± 0.001	
	0.050	0.059 ± 0.005	
	2.000	2.05 ± 0.05	

reaction variables and flow parameters, the optimum reaction conditions and manifold configuration were decided for the determination of traces of cobalt, as shown in Fig. 1. A calibration graph was linear in the concentration range of $0.0\text{--}4.0 \mu\text{g ml}^{-1}$ cobalt with a regression coefficient of 0.9992 (Fig. 6). The relative standard deviation (R.S.D.) for the determination of $1.0 \mu\text{g ml}^{-1}$ cobalt was 0.9% (ten replicate injections), and at all concentration measured, the %R.S.D. of the data was below 5.0. The limit of detection was $0.2 \mu\text{g ml}^{-1}$. The results of the analysis of three synthetic samples are given in Table 1. The sample throughput rate was about 120 h^{-1} .

The procedure of cobalt determination with NRS in the presence of WP by FI method has been tested on a sample of river water after its membrane preconcentration. The results are given in Table 1.

5. Conclusion

The paper demonstrated that the rate of reaction between cobalt and NRS increased sharply by adding WP into reaction solution. This effect

was successfully utilized for development of the FI method for cobalt determination in an acid media. Because of a triple species Co–NRS–WP can be formed, the membrane filtration procedure was used for cobalt preconcentration from river water sample.

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