

Quercetin immobilized on silica gel as a solid phase reagent for tin(IV) determination by using the sorption-spectroscopic method

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Abstract

New chelating sorbents are prepared by 3,3',4',5,7-pentahydroxyflavone adsorption from butanol and acetone–hexane (1:4) solutions, characterized by isotherm of sorption, IR-spectroscopy and studied for pre-concentrating and sorption-spectroscopic determination of Sn(IV). The solid-phase Quercetin with satisfactory analytical characteristics was formed by adsorption from acetone–hexane (1:4) mixture. The quantitative recovery of Sn(IV) from aqueous solution with modified sorbent was observed at pH 1.8–2.2. The tolerance limits of heavy metal ions in the sorption of Sn(IV) are reported. The limit of Sn detection is 0.06 mg l^{-1} . The linearity of calibration graph has been observed up to 1.2 mg l^{-1} . The method has been applied to determine Sn in high purity zinc materials. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Adsorption; Silica gel; Quercetin immobilized; Determination of tin

1. Introduction

The determination of metal ions, tin in particular, at micro and trace level is very important in the context of high purity material development. Graphite furnace atomic absorption spectroscopy (FAAS) is known to be one of the powerful

techniques for Sn determination in alloys [1,2]. However, the necessary detection limit is arrived by previous extraction isolation and enrichment of analyte, that also permits minimizing the matrix effect. Recently, the spectrophotometric (SP) [3] and differential pulse polarographic (DPP) [4] methods on the base of chelating reagents modified with surfactants [3] and microcrystalline naphthalene [4] were reported as an alternative technique for Sn determination. The limits of Sn detection are 0.04 and 0.15 mg l^{-1} , respectively. The solid-phase reagents on the base of modified

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sorbents are found to be simple and cost-effective tools for analytical sampling and sensitive detection of various compounds in complicated objects [5–9]. Quercetin (H_5R) is known to be one of the most effective chelating reagents for spectrophotometric and extraction-spectrophotometric (ESP) determination of Sn(IV) [10,11]. But these methods are time-consuming, poorly selective and require the use of toxic organic solvents. The analytical characteristics of Quercetin were reported to be improved by its immobilization onto the dextran type sorbent (Sephadex-25) [12]. High-dispersed silicas (SG) are one of the best matrices for analytical reagent immobilization because of their specific characteristics [5]. Recently, adsorption of reagents from organic solvents has been reported as an effective and simple method for silica surface modification [7]. This technique has been successfully applied to make SG modified with Morin, the analogue of Quercetin [13].

The solid-phase reagent on the base of SG modified by Quercetin adsorption has been developed. A method of tin pre-concentration from aqueous solution using Quercetin immobilized with subsequent diffuse-reflectance spectroscopic detection was established. The usefulness of the proposed method for Sn determination ($\geq 1.4 \times 10^{-40}\%$) in high purity zinc materials was demonstrated. The results of these investigations are reported in this article.

2. Experimental

2.1. Instrumentation

The absorbance spectra of solutions and reflectance spectra of sorbents were recorded with a Specord M-40 (Carl Zeiss Jena, Germany) UV/Vis spectrophotometer. The function $F(R)$ was calculated according to the equation $F(R) = (1 - R)^2/2R$, where R is the coefficient of diffuse-reflectance of sorbent. The infrared spectra of sorbents were recorded with a UR-20 (Carl Zeiss Jena, Germany) automatic IR photometer. A potentiometer model EV-74 with glass electrode (Gomel, Belarus) was used for pH measurements.

2.2. Reagents and solutions

All chemicals were of analytical reagent and chemical grade. Acetone, butanol, chloroform, ethanol and hexane for liquid chromatography (Merck) were used. Water was purified according to Ref. [14]. Standard solutions of Fe(III), Th(IV), and Zr(IV) were prepared by dissolving $Fe(NO_3)_3$, $Th(NO_3)_4$, and $ZrOCl_2 \cdot 8H_2O$ in 1.0 mol l^{-1} solutions of suitable acids and standardizing according to Ref. [15]. Standard solutions of Sn(IV) and Zn(II) were prepared by dissolving tin granulated GR (Merck) and ZnO in HCl. Sodium chloride (3.0 mol l^{-1}) was prepared by dissolving NaCl in purified water. The standard solutions of metal salts were acidified with hydrochloric acid and further diluted as required. The solution of H_5R in butanol and acetone (1.0 mmol l^{-1}) was obtained by dissolving an appropriate amount of substance. Silica gel (SG) for chromatography (Chemapol, Prague, Czech Republic) was consecutively washed with hydrochloric acid and purified water, then dried at $353 \pm 5 \text{ K}$ for 8 h. The amorphous silica gel (Kalush, Ukraine, specific surface area $S = 300 \text{ m}^2 \text{ g}^{-1}$) was used without preliminary treatment.

2.3. Procedures

The batch technique was used for the study of Quercetin adsorption onto unloaded silica gel so as for metal ions adsorption onto SG loaded with H_5R . The reagent desorption from the surface into aqueous solutions at different pH was also studied by this technique.

2.3.1. Adsorption of reagent onto SG and metal ions onto modified SG

The weighed amount ($0.01\text{--}0.20 \text{ g}$) of SG and modified sorbents was stirred with $5\text{--}20 \text{ ml}$ of $1 \times 10^{-6}\text{--}1 \times 10^{-4} \text{ mol l}^{-1}$ reagent or metal salt solutions for $1\text{--}60 \text{ min}$. The residue of H_5R in solution was controlled spectrophotometrically by absorbance at $\lambda_{\text{max}} = 375 \text{ nm}$ (butanol, $\epsilon_{375\text{nm}} = 2.35 \times 10^4$) and $\lambda_{\text{max}} = 370 \text{ nm}$ (acetone–hexane, $\epsilon_{370\text{nm}} = 2.07 \times 10^4$). The residue of Zr(IV), Th(IV) and Fe(III) in solutions was controlled spectrophotometrically with Chrome Azurol [16], Ar-

senaso III [17], NaSCN [18], respectively. The residue of Sn(IV) in solution was controlled spectrophotometrically with Quercetin [19]. For this purpose the portion of solution obtained after the sorbent separation (3.0 ml) was mixed with 2.0 ml of 5.0×10^{-4} mol l⁻¹ ethanol solution of H₅R. The absorbance of the solutions was measured at 435 nm and $l = 1$ cm. The concentration of Sn(IV) in the solution was determined by means of a calibration graph that was prepared under the same conditions using standard Sn(IV) solution. The equation for the calibration graph was $A_{435} = (-0.01 \pm 0.02) + (1.63 \pm 0.02) \times 10^4 \times C_{\text{Sn(IV)}}$ (mol l⁻¹), $r = 0.998$. The amount of compounds adsorbed on the surface (a , mol g⁻¹) and the coefficient of distribution of Sn(IV) (D , ml g⁻¹) were calculated according to the equations: $a = (C_0 - C)V \times 10^{-3}$ mol g⁻¹; $D = (C_0 - C)V \times C^{-1}$ ml g⁻¹, where C_0 and C were the initial and equilibrium concentrations of adsorbate in the solution (mol l⁻¹); V was the volume of solution (ml); and m was the sorbent mass (g).

2.3.2. Desorption of H₅R from the surface of modified sorbents

The aqueous solutions (10 ml) were acidified with HCl to pH 0–5 and stirred with modified SG (0.2 g) for 1–60 min. The amount of the reagent removed from surface into solution was determined spectrophotometrically by the absorbance of its complex with Zr [20].

2.3.3. Preparation of samples of modified sorbents for IR-spectroscopic measurements

The amorphous SG was used for IR-spectroscopic measurements because of its weak dispersion of IR-radiation. The water adsorbed on SG surface was removed by drying in a vacuum at 295 ± 1 K for 10 h [21].

The weighed amount (0.05 g) of sorbent was stirred for 15 min with 10 ml of solutions containing 0.15 and 0.30 mmol l⁻¹ (butanol) or 0.5 and 2.0 μ mol l⁻¹ (acetone–hexane) of Quercetin. Then sorbents were separated and dried in a vacuum at 341 ± 1 K for 1 h. The amount of reagent adsorbed was (μ mol g⁻¹): 9.2, 14.8 and 0.16, 0.63, respectively.

3. Results and discussion

3.1. Adsorption of Quercetin onto SG from butanol and acetone–hexane solutions

Earlier we loaded Morin onto SG by its adsorption from a mixture of acetone and hexane with the ratio of 1:4 [13]. Butanol is known to be one of the best solvents of Quercetin [22]. Therefore, the adsorption of Quercetin onto SG from butanol and acetone–hexane (1:4) solutions was investigated. The kinetics experiments have shown that the equilibrium of reagent adsorption from butanol onto SG was reached in 5 min. Quercetin adsorption was studied as a function of reagent concentration in solution. The results obtained (Fig. 1, curve 1) testify that the isotherm can be referred to the S-type [23]. Moreover, the data of Fig. 2 show that the significant increase of reagent adsorption is caused by intermolecular attraction of Quercetin molecules in the solution (at $C \geq 1 \times 10^{-4}$ mol l⁻¹), causing it to associate rather than to remain as isolated units [24].

The equilibrium of reagent adsorption from acetone–hexane (1:4) mixture has been reached in 2 min. The isotherm of H₅R adsorption from acetone–hexane presented in Fig. 1 (curve 2) can be referred to L-type [23]. The maximum value of

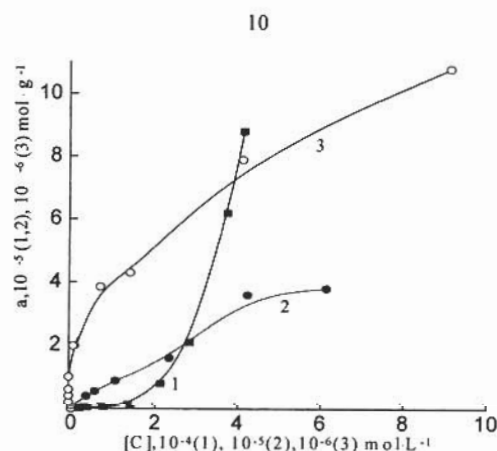


Fig. 1. The isotherm of Quercetin adsorption onto unloaded SG from butanol (1) and acetone–hexane (2) solutions and Sn(IV) onto SG2 (3). $a = 8 \times 10^{-6}$ mol g⁻¹; pH 2.0; $C_{\text{NaCl}} = 1.0$ mol l⁻¹ (3); $T = 292.5 \pm 0.5$ K.

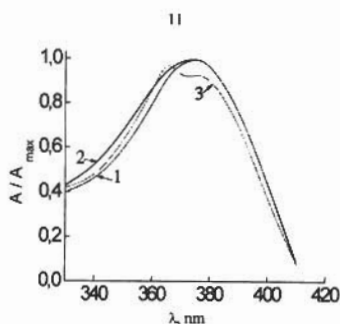


Fig. 2. Standardized absorbance spectra of Quercetin butanol solutions. C , 10^{-4} mol l^{-1} : 0.2 (1), 0.5 (2), 1.0 (3).

reagent adsorption was experimentally found to be 9.4×10^{-6} mol g^{-1} . The diffuse-reflectance spectra of SG modified by reagent adsorption from butanol and acetone–hexane solutions (SG1 and SG2, respectively) are shown in Fig. 3. Taking into consideration the difference in the spectra of modified SG (Fig. 3, curves 4,5) and in the type of isotherms obtained under appropriate conditions (Fig. 1, curves 1, 2) we supposed the influence of solvent on the nature of reagent binding with SG surface. This phenomenon was examined using spectroscopic methods. IR-spectra of SG2 (curves 1–3) and SG1 (curves 4–6) are presented in Fig. 4. It is shown that significant weakening of the intensity of absorption band at 3749 cm^{-1}

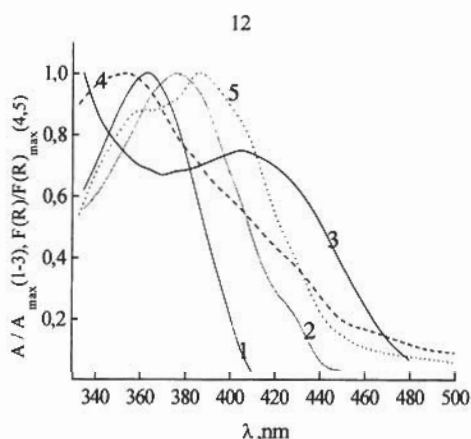


Fig. 3. Absorbance spectra of H_5R and H_4R^- in aqueous ethanol (5%) solution at different pH (1–3) and diffuse-reflectance spectra of SG1 (4) and SG2 (5). $C = 5 \times 10^{-5}$ mol l^{-1} (1–3); pH: 4.9 (1), 9.0 (2), 13.0 (3); $a = 3.4$ μ mol g^{-1} (4,5).

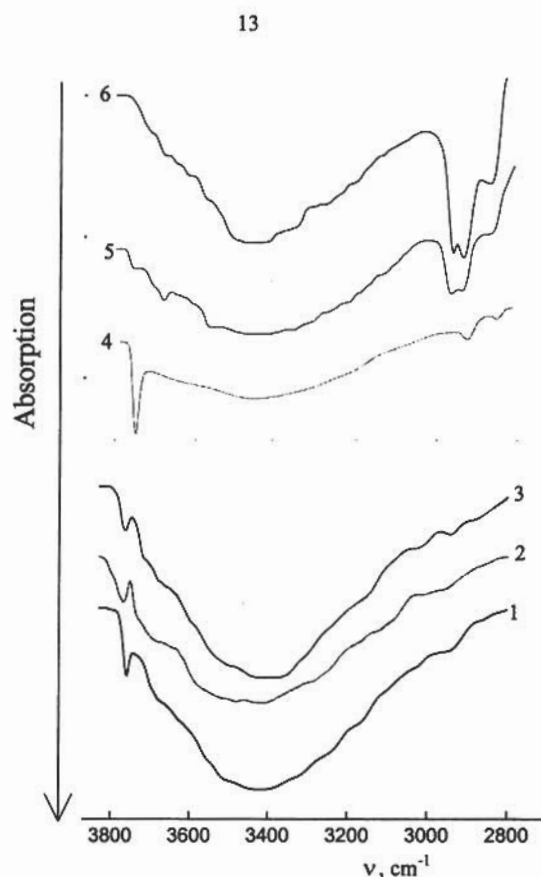


Fig. 4. IR-spectra of SG unloaded (1,4) and Quercetin modified by adsorption from acetone–hexane (2,3) and butanol (5,6) solutions. a , μ mol g^{-1} : 0.158 (2), 0.625 (3), 9.2 (5), 14.8 (6).

belonging to the valence vibration of free surface OH-groups [21] with increasing reagent content on the surface was observed in both cases. This fact indicates that the OH-groups of the SG take part in the fixation of reagent on the surface.

But the L-type of isotherm of Quercetin adsorption from acetone–hexane solution may be a result of participation of carbonyl- as well as OH-groups of H_5R in the reagent grafting on the surface. The appearance of a short-wave maximum in diffuse-reflectance spectra of SG2 (Fig. 3, curve 5) confirms this fact.

Therefore, the results indicate that the effect of solvent on the nature of binding of modifying agent with the silica surface may be essential. So

the analytical characteristics of solid-phase reagents obtained by Quercetin adsorption from various solvents should differ.

3.2. Desorption of Quercetin by hydrochloric acid

To examine the usefulness of SG1 and SG2 in analytical practice, the desorption of Quercetin from the surface as a function of HCl concentration, volume of solution and time of phases contact has been studied. It was found that the reagent was completely removed from the surface of SG1 under optimum conditions of its complexing with polyvalence elements (pH 0–5). So, the SG1 application as a solid-phase reagent proved to be impossible. However, the removal of reagent from the SG2 under the same conditions was found to be less than 5%. Moreover, the procedure of SG2 modification was simple and rapid. These properties combined with the high adsorption capacity of SG2 ($a_{\max} = 3.5 \times 10^{-5} \text{ mol g}^{-1}$) and stability (solid-phase reagent was stable for more than 6 months) testified to the suitability of SG2 for analytical practice.

3.3. Interaction of metal ions with Quercetin immobilized

In order to apply the SG2 for metal ion determination, the adsorption of polyvalence elements forming colored or fluorescent complexes with Quercetin in the solution was studied.

The Th(IV) and Fe(III) recovery with SG2 under optimum conditions of complex formation in solution was found to be caused by hydrolytic sorption but not complexing with immobilized reagent. Zirconium (IV) interacts with Quercetin in the solution at pH 1.0 [25]. The formation of complexes $[\text{ZrO}(\text{H}_4\text{R})]^+$ and $[\text{ZrO}(\text{H}_4\text{R})_2]$ on the sorbent and in the equilibrium solution was found spectrophotometrically. But the analytical application of SG2 for Zr(IV) determination using diffuse-reflectance spectroscopy is limited with a low analytical signal at its concentration $\leq 1 \times 10^{-5} \text{ mol l}^{-1}$.

Sn(IV) is known to interact with Quercetin in solution at pH 1–3 [10]. So, its sorption onto SG2 was studied under these conditions by addition of

$1.0 \text{ mol l}^{-1} \text{ NaCl}$ (to prevent the hydrolysis). The recovery of Sn(IV) with SG2 at pH 1.8–2.2 was found to be quick and quantitative. The maximum coefficient of Sn(IV) distribution was $1 \times 10^6 \text{ ml g}^{-1}$ at $V:m = 100 \text{ ml g}^{-1}$. The isotherm of Sn(IV) adsorption is presented in Fig. 1 (curve 3). H-type of isotherm testifies to complexation between the Sn(IV) and immobilized reagent. The absorbance spectra of solutions of complexes and diffusion reflectance spectrum of SG2 treated with solution of Sn(IV) are presented in Fig. 5. The comparison of the spectra testified to $[\text{Sn}(\text{H}_3\text{R})]^{2+}$ formation on the surface. In contrast to zirconium the tin adsorption was not accompanied with complexing in aqueous solution. This phenomenon may be a result of Sn(IV) interaction with immobilized reagent through the 3',4'-orthodiphenolic group [5,26]. This group is unlikely to take part in reagent grafting on the surface because of intramolecular bound hydrogen.

The diffuse-reflectance spectra of SG2 treated with solutions with different Sn(IV) concentrations are presented in Fig. 6. It was shown that the intensity of signal at 420 nm increased with increasing tin concentration in solution. The equation of the calibration graph was $\Delta F(R)_{420} = (-0.03 \pm 0.05) + (2.66 \pm 0.01) \times C(\text{mg l}^{-1})$, $r = 0.998$. The detection limit (blank + 3σ) was 0.06 mg l^{-1} , where σ is the standard deviation of blank estimation. The linearity of the calibration graph was observed up to 1.2 mg l^{-1} .

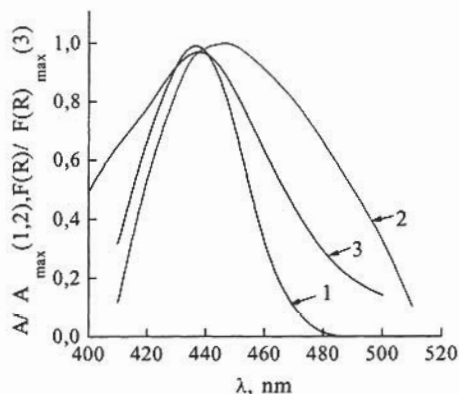


Fig. 5. Standardized absorbance spectra of aqueous ethanol (40%) solutions of complexes with the ratio Sn(IV)/R = 1:1 (1) and 1:2 (2) and diffuse-reflectance spectra of SG2 treated with Sn(IV) solution. $C_{\text{HCl}} = 0.01 \text{ mol l}^{-1}$ (3).

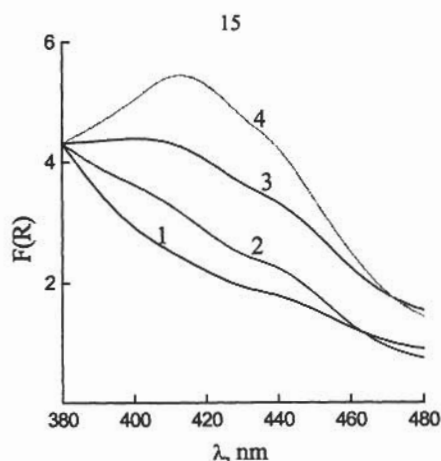


Fig. 6. The diffuse-reflectance spectra of SG2 treated with Sn(IV) solutions. $C_{\text{HCl}} = 0.01 \text{ mol l}^{-1}$, $C_{\text{Sn}}, 10^{-6} \text{ mol l}^{-1}$: 0 (1), 2 (2), 6 (3), 10 (4); $C_{\text{NaCl}} = 1.0 \text{ mol l}^{-1}$; $V = 10 \text{ ml}$; $m = 0.100 \pm 0.001 \text{ g}$; $a = 6.67 \mu\text{mol g}^{-1}$.

3.4. Interference from foreign ions

The interference from Zn(II), Cd(II), Fe(III), Pb(II), Cu(II), Zr(IV) on Sn(IV) adsorption and the value of the analytical signal in diffuse reflectance spectra were examined. No interference was observed for the following ions (divisible excesses): Zn(10^5), Cd, Pb(10), Cu(5), Zr(2), Fe (20, in the presence of ascorbic acid). To check the accuracy of the proposed method, the standard and model solutions were examined. The results

Table 1
The results of tin determination ($n = 6$, $P = 0.95$)

<i>N</i>	Sample	Added Sn (mg l^{-1})	Analysed Sn (mg l^{-1})
1	Standard solution	0.47	0.49 ± 0.05
2	Model solution	0.24	0.27 ± 0.05
3	Zn 99.995	1.1×10^{-3a}	$(1.1 \pm 0.2) \times 10^{-3}$
4	Zn 99.95	1.1×10^{-3a}	$(1.0 \pm 0.3) \times 10^{-3}$

Concentration (mol l^{-1}): 2: Zn (0.8), Pb (4.8×10^{-5}), Cd (3.8×10^{-4}), Fe (3.0×10^{-5}), Cu (2.0×10^{-6}); passport content (%): 3: Zn (99.995), Pb (0.03), Cd (0.02), Fe (0.002), Cu (0.001); 4: Zn (99.95), Pb (0.02), Cd (0.01), Fe (0.01), Cu (0.002), As (0.0005).

^a Percent.

are presented in Table 1. One can see the relative standard deviation (RSD) did not exceed 0.1.

4. Application of the method

The proposed method was applied to tin determination in high purity zinc. The sample of alloy ($2.0000 \pm 0.0001 \text{ g}$) was dissolved in 6.0 ml of conc. HCl by addition of 1 ml of 50% H_2O_2 . The solution obtained was boiled until H_2O_2 was removed. After cooling to room temperature, the solution was placed in a volumetric flask and made up to the total volume of 50 ml with 1.0 mol l^{-1} NaCl (the pH of the solution obtained was 2.0). The portion of solution (10 ml) was mixed with 1.5 ml of saturated ascorbic acid solution and stirred with $0.10 \pm 0.01 \text{ g}$ of SG2 for 10 min. Sorbent was centrifuged and dried at $335 \pm 1 \text{ K}$. The coefficient of diffuse-reflectance of sorbent at 420 nm was recorded. The Sn concentration was determined by means of a calibration graph which was prepared under the same conditions using of the standard Sn solution (10 ml) containing $(0, 0.1, 0.2, 0.4, 0.8 \text{ and } 1.0) \times 10^{-5} \text{ mol l}^{-1}$ Sn(IV), 1.0 mol l^{-1} NaCl, 0.7 mol l^{-1} Zn(II). Zn(II) and NaCl were added to create constant ionic strength in the solution. The pH 2.0 was adjusted by addition of HCl. The equation of the calibration graph was $\Delta F(R)_{420} = (-0.03 \pm 0.05) + (1.06 \pm 0.03)\omega(10^{-3}\%)$, $r = 0.998$. The detection limit was $1.4 \times 10^{-4}\%$.

The results are presented in Table 1. The data confirm the usefulness of the development solid-phase reagent for tin determination in such conditions.

5. Comparison of developed method with other techniques

The analytical characteristics of the sorption-spectroscopic method of tin determination using immobilized Quercetin are compared with those of other reported methods in Table 2. It is evident that the sensitivity of the developed method is higher or comparable with that of SP [26], ESP [26], DPP [4] and sorption-luminescent methods [27]. No use of toxic compounds is an advantage

Table 2
Comparison the chemical-analytical characteristics of the methods of tin determination

Method	Reagent/support	Interference from foreign ions (divisible excesses)	Detection limit (mg l ⁻¹)	Reference
SP	Pyrocatechol violet + surfactant	Al, Cd, Co, Mg, Ca, Mn, Ni, Pb (1250); Cu (50); NaCl (10); Fe (2.5); Bi, Sb, Ti, Mo, tartrate, citrate, I ⁻	0.04	[3]
SP	Phenilfluoron	PO ₄ ³⁻ , Ti, Sb, As, Cr, Fe	0.2 ^b 5 × 10 ^{-4a}	[26]
ESP	Quercetin	Sb	0.2	[26]
Sorption-luminescent	Morin/Sefadex G-25	Cr(VI), Hf(1); Be, Al, Ga, In, Tl, Sc, P3E, V, Th, Ti, Ge, V, Nb, Ta, Te, Bi, Mo, W, Fe, Cu, Cr(III) (≥ 500)	0.5	[27]
Sorption-spectroscopic	Quercetin/SG	NaCl (10 ⁷); Zr (1); Zn (10 ⁵), Cd, Pb (10), Cu (5), Zr (2), Fe (20, in the presence of ascorbic acid)	0.06	Developed
DPP	IA/naphthalene	—	1.4 × 10 ^{-4a}	
FAAS	—	—	0.15 0.07 1 × 10 ^{-3a}	[4] [2]

IA, ionic associate of tetradecyldimethylbenzylammonium with 2-nitroso-1-naphthol-4-sulfonic acid.

^a Percent in alloys.

^b After pre-concentration onto MnO₂.

of the proposed procedure. The low chloride effect and short time of analysis (the time of the single determination ≤ 30 min) are other advantages of solid-phase Quercetin. In comparison with FAAS [2] the technique using immobilized Quercetin is simple and cost-effective.

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