

## A Novel, Donor-Active Solvent-Assisted Liquid-Phase Microextraction Procedure for Spectrometric Determination of Zinc

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O presente trabalho descreve o uso de microextração em fase líquida com um solvente doador-ativo para a determinação espectrofotométrica de zinco, em 570 nm, usando a reação com tiocianato e com o reagente brometo de 2-[2-(5-dimetilamino-2-tiofenil)-vinil]-1,3,3-trimetil-3H-indolium (DTVTI). As condições experimentais ótimas foram estabelecidas usando  $\text{NH}_4\text{SCN}$   $0,02 \text{ mol L}^{-1}$  e DTVTI  $4 \times 10^{-5} \text{ mol L}^{-1}$ . Estudaram-se ainda vários solventes extratores, separados e em misturas, com diferentes promotores, sendo selecionada a mistura de tolueno como solvente de extração e tributílfosfato como solvente doador-ativo na razão de 4:1 v/v. O sistema mostrou resposta linear até a concentração de  $2,62 \text{ mg L}^{-1}$  de zinco com um limite de detecção de  $0,09 \text{ mg L}^{-1}$ . O método desenvolvido foi aplicado na determinação de zinco em suplementos dietéticos.

Based on the reaction of Zn(II), thiocyanate and 2-[2-(5-dimethylamino-thiophen-2-yl)-vinyl]-1,3,3-trimethyl-3H-indolium bromide (DTVTI), a donor-active solvent-assisted liquid-phase microextraction procedure followed by spectrophotometric determination of zinc at 570 nm was developed. The optimum experimental conditions were investigated and found to be as follows: concentration of  $\text{NH}_4\text{SCN}$   $0.02 \text{ mol L}^{-1}$ , concentration of DTVTI  $4 \times 10^{-5} \text{ mol L}^{-1}$ . Various extraction solvents were studied alone as well as in mixtures with different improvers, and a mixture of toluene as the extraction solvent and tributylphosphate as the donor-active solvent in a 4:1 v/v ratio was selected. The calibration plot was linear up to  $2.62 \text{ mg L}^{-1}$  of zinc with limit of detection  $0.09 \text{ mg L}^{-1}$ . The developed procedure was applied for zinc determination in dietary supplements.

**Keywords:** zinc, donor-active solvent-assisted liquid-phase microextraction (DAS-LPME), dietary supplements, spectrophotometry

### Introduction

Zinc is among the most commonly used metals and has a number of applications in industry. Zinc and its compounds are frequently used for galvanising, for the production of alloys such as brass and bronze, and as pigments in paints, among other uses. Zinc is also an essential trace element and is indispensable for the functioning of numerous enzymes.<sup>1-3</sup> It is naturally present in some foods and also available in dietary supplements.<sup>4</sup>

Currently we can see several trends in analytical chemistry, including miniaturization, development of novel methods that comply with the requirements of green chemistry, as well as automation. Liquid-liquid extraction, one of the oldest sample pre-treatment techniques, is no exception to these trends.<sup>5,6</sup> Liquid-phase microextraction has now been coupled with the majority of analytical instrumentation,<sup>7-10</sup> however, the use of spectrophotometry as a detection technique is sometimes difficult,<sup>11,12</sup> primarily because the micro-volume of the organic phase is not sufficient for performing an absorbance measurement in conventional UV-Vis spectrophotometers.<sup>10</sup> On the

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other hand, traditional molecular spectrophotometry is not old-fashioned;<sup>13</sup> it is still one of the most commonly employed detection techniques<sup>14-15</sup> in analytical chemistry and is frequently used for the determination of metals after a complex-formation step.<sup>16</sup>

One can find only a limited number of papers devoted to microextraction procedures for the determination of zinc, and the majority of these coupled with flame atomic absorption spectrometry or inductively coupled plasma-optical emission spectrometry.<sup>17-19</sup> Therefore, in a continuation of our previous endeavors in the development of novel sample pre-treatment techniques,<sup>20-24</sup> we herein offer a microextraction procedure coupled with the UV-Vis spectrometric determination of zinc. The method is based on the formation of an ion associate between Zn(II), thiocyanate and 2-[2-(5-dimethylamino-thiophen-2-yl)-vinyl]-1,3,3-trimethyl-3*H*-indolium bromide (DTVTI) that is extractable by a mixture of solvents.

## Experimental

### Reagents

All chemicals and solvents used were of analytical reagent grade.  $\text{ZnSO}_4 \times 7\text{H}_2\text{O}$  and  $\text{NH}_4\text{SCN}$  were purchased from Sigma-Aldrich. The DTVTI reagent was a kind gift from Dr. Joseph S. Balogh. Distilled water with conductivity of  $2.5 \mu\text{S cm}^{-1}$  was used throughout the work. A stock solution of  $1 \times 10^{-3} \text{ mol L}^{-1} \text{ Zn}^{2+}$  was prepared by dissolving 0.0289 g  $\text{ZnSO}_4 \times 7\text{H}_2\text{O}$  in water (to avoid hydrolysis, a few drops of  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  were added) and filling it up to 100 mL. The working solution of  $1 \times 10^{-4} \text{ mol L}^{-1}$  was prepared by dilution of the stock solution. The  $0.5 \text{ mol L}^{-1} \text{ SCN}^-$  solution was prepared by dissolving 3.8055 g of  $\text{NH}_4\text{SCN}$  in water and filling it up to 100 mL. The  $1 \times 10^{-3} \text{ mol L}^{-1}$  solution of DTVTI prepared by its dissolving 0.0391 g in water and filling it up to 100 mL. The acidity of the aqueous phase was adjusted by addition of  $0.5 \text{ mol L}^{-1} \text{ H}_2\text{SO}_4$  or  $0.2 \text{ mol L}^{-1} \text{ HOAc-NH}_4\text{OH}$  buffer solutions.

### Apparatus

Spectrophotometric measurements were carried out using a Lightwave II UV/Vis spectrophotometer (Biochrom Ltd., United Kingdom) equipped with quartz cell of appropriate path length. An ORION 720A<sup>+</sup> pH meter with a glass electrode was used for pH measurements. Centrifugation was performed using a CN-2060 LED & Multi-function type centrifuge (MRC Ltd., Israel). NMR spectra were recorded in methanol- $\text{d}_4$  at room temperature with a Bruker Avance DRX-500 spectrometer. The

structure of DTVTI was determined by the comprehensive one- and two-dimensional NMR method. Chemical shifts were given on the  $\delta$ -scale and were referenced to the solvent (methanol- $\text{d}_4$ ;  $\delta_{\text{C}} = 49.15$  and  $\delta_{\text{H}} = 3.31$ ). In the  $^1\text{D}$  measurement ( $^1\text{H}$ , APT), 64 K data points were used for the FID. The pulse programs for all experiments [gs-COSY, gs-HMQC and gs-HMBC) were taken from the Bruker software library.

### Microextraction procedure

Various volumes of Zn(II) working solution (0; 0.3; 0.5; 0.8; 1.0; 1.5; 2.0) were placed into conical centrifugal tubes and followed by the addition of 0.2 mL of  $0.5 \text{ mol L}^{-1} \text{ SCN}^-$  and 0.2 mL of  $1 \times 10^{-3} \text{ mol L}^{-1}$  DTVTI and water up to 5 mL. After each reagent was added, the mixture was gently shaken. Then 0.5 mL of a mixture of toluene (acting as extraction solvent) and tributylphosphate (acting as donor-active solvent) in a 4:1 (v/v) ratio was rapidly injected into the aqueous phase using a microsyringe; the mixture was then shaken gently a few times. Afterwards, centrifugation was carried out at 3000 rpm for 2 min, and the organic phase at the top of the aqueous phase (approx. 250  $\mu\text{L}$ ) was withdrawn using a microsyringe and placed into a quartz cell with optical path of 1 mm for the absorbance measurement at 570 nm.

### Sample preparation

The samples of dietary supplements were bought in a local supermarket. The content of samples (except for zinc) was: Sample 1: vitamin C; Sample 2: Ca, Mg; Sample 3: proteins, sugars, fats, vit. B5, vit. B6, vit. B9, vit. D3, biotin, L-cysteine, L-metionine. One or two tablets containing Zn(II) were crushed in a mortar, dissolved in water, exposed to ultrasonication (10-20 min) to obtain a clear solution and filled up to 100 mL in a volumetric flask. The aliquots of the sample were placed to the test tube and determination took place as described in Microextraction procedure section.

## Results and discussion

### Investigation of experimental conditions

Various parameters that can significantly affect the formation and extraction of the ion associate, such as pH, concentration of thiocyanate and dye reagent as well as type and volume of solvents, were investigated. A series of experiments was carried out, in which the concentration of one parameter was altered and the concentration of other components of the system were kept constant.

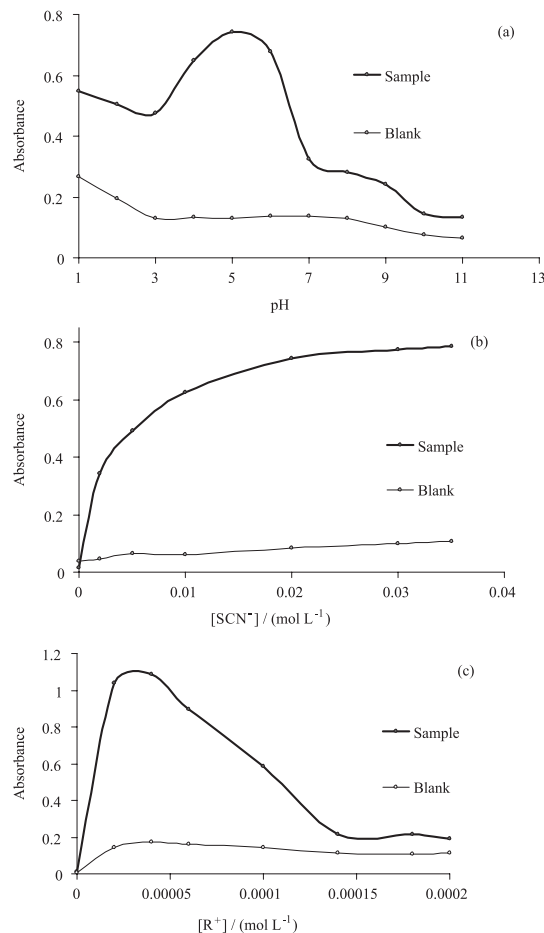
Figure 1a shows the effect of pH on the extraction of the ion pair. The highest absorbance of the extracted ion pair, and simultaneously the lowest absorbance of the blank is observed at pH 5-6. The obvious decrease at lower pH values can be ascribed probably to the formation of HSCN when  $\text{Zn}(\text{NCS})_3^-$  is not able to form. On the other side, decrease in the absorbance values above pH 6 is probably due to the hydrolysis of  $\text{Zn}(\text{NCS})_3^-$  and formation of  $[\text{Zn}(\text{NCS})_2(\text{OH})]^-$ , which, due to the loss of  $\text{SCN}^-$  is not able to form an extractable form with the dye, and thus can not be extracted.

Apart from pH, another important parameter is the optimization of ligand concentration. For this reason, the effect of  $\text{SCN}^-$  concentration up to  $0.035 \text{ mol L}^{-1}$  was investigated. Figure 1b shows that higher concentrations of  $\text{SCN}^-$  ions lead to higher absorbance values up to  $0.03 \text{ mol L}^{-1}$ . Further addition results in lower absorbance values, what can be attributed to the formation of complexes of zinc with higher ligand number ( $[\text{Zn}(\text{NCS})_4]^{2-}$ ) that are non extractable. Thus, the concentration of  $0.02 \text{ mol L}^{-1}$  of  $\text{NH}_4\text{SCN}$  was chosen.

The effect of the dye reagent was also investigated up to  $2 \times 10^{-4} \text{ mol L}^{-1}$  and absorbance increased to the concentration  $4 \times 10^{-5}$ - $6 \times 10^{-5} \text{ mol L}^{-1}$ . Further addition of the dye resulted in the association of the molecule of the dye as the effect of  $\text{SCN}^-$  ions, thus the concentration of the dimer form of the dye increases, what in consequence, leads to the decrease in concentration of the reactive form of the dye as Figure 1c shows. Thus, a concentration of the dye reagent as high as  $4 \times 10^{-5} \text{ mol L}^{-1}$  were selected for further experiments.

#### Effect of the organic solvent

Besides the above-mentioned variables, the nature of the organic solvent used can also significantly influence the extraction efficiency. The nature of the analyte has an equally important influence. Some metal ions (M), zinc among them, are able to form coordinatively saturated complexes only in the presence of a relatively high concentration of ligand, such as, for example,  $\text{SCN}^-$  when the  $[\text{M}(\text{NCS})_4]^{2-}$  complex is formed. These complexes cannot be extracted in the form of ion associates with dye reagents by using organic solvents. In contrast, at lower concentrations of ligand, only a hydrated coordinatively unsaturated complex  $[\text{M}(\text{NCS})_3 \times \text{H}_2\text{O}]^-$  is formed which can not be extracted by inert solvents due to the presence of water. Nevertheless, such an extraction can be done easily with the use of donor-active solvents that have the ability to block or push water away from the ion associate, like, for example, tributylphosphate or cyclohexanone.

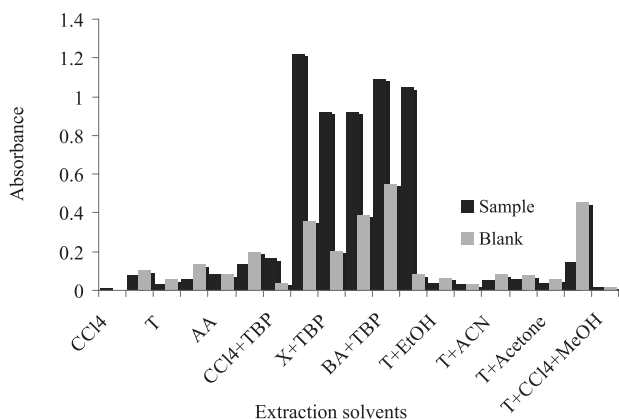


**Figure 1.** Effect of pH (a), thiocyanate (b) and DTVTI (c).  $4 \times 10^{-5} \text{ mol L}^{-1}$  Zn; toluene-tributylphosphate 4:1 (v/v);  $V_{\text{aq}} = 5 \text{ mL}$ ,  $V_{\text{org}} = 500 \mu\text{L}$ ;  $\lambda = 570 \text{ nm}$ ;  $l = 0.1 \text{ cm}$ ; (a)  $0.02 \text{ mol L}^{-1} \text{ NH}_4\text{SCN}$  and  $8 \times 10^{-5} \text{ mol L}^{-1}$  DTVTI; (b)  $8 \times 10^{-5} \text{ mol L}^{-1}$  DTVTI; (c)  $0.02 \text{ mol L}^{-1} \text{ NH}_4\text{SCN}$ .

These solvents must fulfill certain requirements, namely a low dielectric constant and better solubility in inert solvent than in water (tributylphosphate with its Gutmann's donor-activity is  $23.7 \text{ kcal mol}^{-1}$  and dielectric constant 6.8). Unfortunately, application of donor-active solvent itself causes an unfavorable increase in the absorbance of the blank test, and there is no difference between the blank and the sample absorbance. This means that both inert and active solvents are themselves inapplicable for the extraction of ion associates formed by coordinatively unsaturated complex and dye reagents. In this case, a mixture of inert (toluene, benzene, hexane, carbon tetrachloride) and active (esters-butylacetate, amylacetate, tributylphosphate, and ketones-cyclohexanone, methyl isobutyl ketone) solvents is commonly employed. The addition of only small amount of donor-active solvent to an inert solvent can act synergistically by increasing the extraction efficiency while at the same time not affecting the value of blank test. Synergism is well known and often applied in extractive spectrophotometric methods and can

be achieved, for example, by the addition of another ligand or reagent<sup>23,24</sup> as well as by the addition of another solvent.<sup>25</sup>

Therefore, besides the solvent itself (carbon tetrachloride, benzene, toluene, xylene, amyl acetate, butyl acetate), mixtures of various extraction solvents with tributylphosphate and mixtures of toluene with various improvers (ethanol, methanol, acetonitrile, tetrahydrofuran, cyclohexanone, tributylphosphate) were tested (Figure 2). As could be expected, the extraction solvent by itself is only capable of extracting the ion associate slightly. The best result (the highest value of the analytical signal and simultaneous lowest value of the blank) was obtained using a mixture of toluene and tributylphosphate in a 4:1 v/v ratio (Figure 2). Therefore, this mixture was chosen for further experiments. Tributylphosphate serves as a donor-active solvent since it is able to push the molecules of water away from the coordination sphere of the complex (see Reaction chemistry Section and reference 26), thus enhancing the extraction efficiency. Tributylphosphate participates in the solvation of the unsaturated anionic complex typical for an extraction based on the hydration-solvation mechanism.<sup>27</sup>

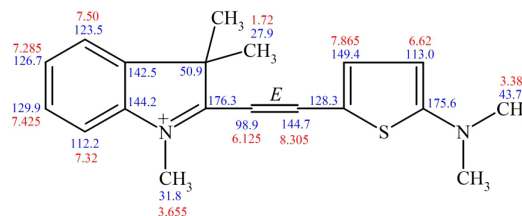


**Figure 2.** Effect of the solvents.  $4 \times 10^{-5}$  mol L<sup>-1</sup> Zn; 0.02 mol L<sup>-1</sup> NH<sub>4</sub>SCN;  $4 \times 10^{-5}$  mol L<sup>-1</sup> DTVTI; V<sub>aq</sub> = 5 mL, V<sub>org</sub> = 500 μL; λ = 570 nm; l = 0.1 cm; B: benzene; T: toluene; X: xylene; AA: amyl acetate; BA: butyl acetate; TBP: tributylphosphate; EtOH: ethanol; MeOH: methanol; ACN: acetonitrile; THF: tetrahydrofuran; CHN: cyclohexanone.

### Reaction chemistry

On the basis of <sup>1</sup>H NMR, APT, HMQC and COSY spectra, we were able to identify the *N*-methyl, geminal *C*-methyls, geminal *N*-methyls 1,2-disubstituted benzene ring, the thienyl ring and the –CH=CH– group of the molecule of DTVTI reagent (Figure 3). We used the HMBC spectrum to confirm the connection of the sub-units of the DTVTI compound.

The *N*-methyl signal (δ<sub>H</sub> = 3.655 ppm) and the geminal methyl signal (δ<sub>H</sub> = 1.72 ppm) show cross-peaks with the signal at δ<sub>C</sub> = 176.3 ppm, proving the indole-2 position of the

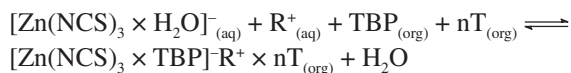
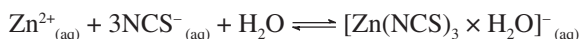


**Figure 3.** The structure and <sup>1</sup>H and <sup>13</sup>C NMR signal assignments of DTVTI. Red/blue coloured numbers indicate the <sup>1</sup>H/<sup>13</sup>C chemical shifts.

quaternary carbon atom. The signal at δ<sub>C</sub> = 50.9 ppm (C-3) is marked out by the signals at δ<sub>H</sub> = 7.50 ppm and 6.125 ppm, thus verifying the connection of the 1,2-disubstituted benzene ring and the –CH=CH– group. The 8.305 ppm/149.4 ppm, 6.62 ppm/175.6 ppm and 3.38 ppm/175.6 ppm HMBC correlation justify the existence of the dimethylaminothienyl group in the molecule.

One of the fundamental steps in the extraction of zinc ion associate is the formation of a complex between the Zn<sup>2+</sup> and NCS<sup>-</sup>. It is well known that thiocyanate and isothiocyanate ions are linear in structure, which is why the distribution of the negative charge on them is approximately equal between the S and the N atoms (Q<sub>S</sub> = -0.48, Q<sub>N</sub> = -0.51).<sup>28</sup> It is also well known that with Pearson's "hard acid" metal ions, the ambidentate SCN<sup>-</sup> anion binds at the N atom of the thiocyanate to form the complex, while in the case of Pearson's "soft acid" metal ions it binds at the S atom. Zn(II) is a borderline case as a Pearson's borderline Lewis acid,<sup>29,30</sup> but according to Klopman's hardness scale for complex compounds, it belongs among the "hard acid" metal ions (for example Zn(II) is -0.60 and Hg(II) is -4.40).<sup>30,31</sup> This has also been confirmed by a large number of spectrochemical measurements<sup>28</sup> in which complex formation of Zn<sup>2+</sup> with NCS<sup>-</sup> in aqueous solution takes place with binding at the N atom.

Therefore, in our opinion, the formation and extraction of the ion associate may be expressed by the following scheme:



where aq and org mean the aqueous and organic phases, respectively, and R is DTVTI reagent, TBP is tributylphosphate, and T stands for toluene.

### Matrix effect

The matrix effect was studied by spiking commercially available mineral waters and juices with Zn(II) at different

**Table 1.** Determination of zinc in dietary supplements by the proposed method<sup>a</sup> and by the reference method<sup>b</sup> (n = 5)

Content of sample (mg per tablet)	Calculated / (mg L <sup>-1</sup> )	Determined <sup>a</sup> / (mg L <sup>-1</sup> )	RSD / %	R / %	Determined <sup>b</sup> / (mg L <sup>-1</sup> )
Vitamin C (100), Zn (15)	0.70	0.70 ± 0.08	9.2	100	0.69 ± 0.04
	1.20	1.16 ± 0.09	6.2	96.6	1.22 ± 0.06
	2.00	2.00 ± 0.10	4.0	100	1.97 ± 0.05
Ca (333.90), Mg (133.50), Zn (8.00)	0.70	0.71 ± 0.07	7.9	101.4	0.72 ± 0.03
	1.20	1.20 ± 0.03	2.0	100	1.18 ± 0.04
	2.00	1.99 ± 0.09	3.6	99.5	2.00 ± 0.04
Proteins (207), sugars (11.5), fats (6.0), vit. B5 (9.0), vit. B6 (1.0), vit. B9 (0.1), vit. D3 (0.0025), biotin (0.225), Zn (7.5), L-cysteine (150.0), L-methionine (50.0)	0.70	0.70 ± 0.06	6.9	100	0.71 ± 0.03
	1.20	1.20 ± 0.06	4.0	100	1.23 ± 0.05
	2.00	1.99 ± 0.08	3.2	99.5	2.00 ± 0.06

concentration levels and analysing them using the suggested procedure. The results obtained showed good precision and accuracy of the determination, with no matrix interference (RSD values ranging from 1.5 to 4.2% and recoveries ranging from 98 to 102%).

#### Analytical performance

Applying the optimized experimental conditions, a calibration plot was constructed using five concentration levels up to 2.62 mg L<sup>-1</sup> Zn. For each level, three replicate extractions and determinations were carried out. The regression equation for the calibration curve was  $A = 0.422C + 0.0934$ , where A is the absorbance and C is the concentration of Zn(II) in mg L<sup>-1</sup>. The experimental results showed a good linear relationship between absorbance and the zinc concentration, with a correlation coefficient ( $R^2$ ) of 0.9944. The limit of detection calculated from the regression equation according to the International Conference on Harmonization,<sup>32</sup> using the standard deviation of the blank

samples was found to be 0.099 mg L<sup>-1</sup>. The suggested method was applied to the analysis of dietary supplements and results were compared with the reference method (ICP-OES, 213.856 nm). Five replicate analyses were performed for each sample. Satisfactory results were obtained, with recoveries ranging from 96.6 to 101.4%, therefore, indicating that the sample matrix does not significantly influence the determination. The relative standard deviation (RSD) values range from 2.0 to 9.2% (Table 1).

The efficiency of the presented method was compared with those of other reported methods (Table 2), and it can be observed that the analytical performance of the developed donor-active solvent-assisted liquid-phase microextraction (DAS-LPME) method is comparable with the other reported methods based on spectrophotometric detection. It should be noted that in some of the techniques mentioned, detection systems such as flame atomic absorption spectrometry, long liquid waveguide capillary cell and spectrofluorimetry were used which are essentially more sensitive than spectrophotometry.

**Table 2.** A comparison of the suggested method with other methods reported in literature for determination of zinc

Reagent	Mode	Detection technique	Extraction solvent	Linear range	Detection limit	Sample	Ref.
Zincon	FIA	UV-Vis	–	0.2-9.7 mg L <sup>-1</sup>	60 µg L <sup>-1</sup>	vitamin formulations	33
Zincon	FIA	UV-Vis	–	0.2-9.7 mg L <sup>-1</sup>	60 µg L <sup>-1</sup>	pharmaceutical preparations	34
4-(2-Thiazolylazo) resorcinol	Batch	UV-Vis	–	0.10-1.31 mg L <sup>-1</sup>	–	water samples	35
2,6-bis(1-Hydroxy-2-naphthylazo)pyridine	Batch	UV-Vis	–	0.19-1.0 mg L <sup>-1</sup>	–	food and milk samples	36
N-ethyl-3-carbazolecarboxaldehyde-3-thiosemicarbazone	Batch	UV-Vis	Benzene	0.4-6.0 mg L <sup>-1</sup>	–	foods	37
1-(2-Pyridylazo)2-naphthol	Batch	UV-Vis (HPSAM)	–	0.2-25 mg L <sup>-1</sup>	–	alloys	38
2,4-Dihydroxybenzaldehyde isonicotinoyl hydrazone	Batch	UV-Vis (DS)	–	0.10-1.50 mg L <sup>-1</sup>	–	waters and pharmaceuticals	39
Zincon	Sensor	UV-Vis	–	0.76-30.6 µmol L <sup>-1</sup>	10.5 µg L <sup>-1</sup>	powdered milk and hair samples	40

Table 2. continuation

Reagent	Mode	Detection technique	Extraction solvent	Linear range	Detection limit	Sample	Ref.
Zincon	MSFIA	UV-Vis (LWCC)	–	Up to 0.1 mg L <sup>-1</sup>	2	waters	41
1-Naphthylethylenediamine	FIA	UV-Vis	–	0.5-2.5 mg L <sup>-1</sup>	200 µg L <sup>-1</sup>	plant materials	42
Di-2-pyridyl ketone salicyloylhydrazone	FIA	UV-Vis	–	0.217-4.60 mg L <sup>-1</sup>	48.8 µg L <sup>-1</sup>	biological and pharmaceutical samples	43
2-(5-Nitro-2-pyridylazo)-5-[N-propyl-N-(3-sulfopropyl)amino]phenol	FIA	UV-Vis	–	0.01-1 mg L <sup>-1</sup>	4.0 µg L <sup>-1</sup>	serum	44
8-Hydroxyquinoline	Batch	FAAS	[HPy][PF <sub>6</sub> ]	0.8-33 µg L <sup>-1</sup>	0.22 µg L <sup>-1</sup>	water and milk samples	45
1-(2-Thiazolylazo)-2-naphthol	FIA	UV-Vis (LED)	–	0.05-0.85 mg L <sup>-1</sup>	9 µg L <sup>-1</sup>	pharmaceutical preparation	46
5-(8-Hydroxy-2-quinolinylmethyl)-2,8-dithia-5-aza-2,6-pyridinophane	FIA	fluorimetry	hexanol	0.025-4.53 mg L <sup>-1</sup>	2.3 µg L <sup>-1</sup>	human hair, human serum and two inorganic sludge samples	47
1-(2-Pyridylazo)-2-naphthol	Batch	FAAS	1-dodecanol (USAE-SFODME)	0.02-0.45 mg L <sup>-1</sup>	0.79 µg L <sup>-1</sup>	waters	48
8-Hydroxy-7-(4-sulfo-1-naphthylazo)-5-quinoline sulfonic acid	Batch	fluorimetry	–	50-400 ppb	7 ppb	drinking water, hair and milk samples	49
2-[2-(5-Dimethylamino-2-thienyl)-vinyl]-1,3,3-trimethyl-3H-indolium bromide	Batch	UV-VIS	toluene-TBP	Up to 2.62 mg L <sup>-1</sup>	99 µg L <sup>-1</sup>	dietary supplements	This work

DS: derivative spectrophotometry; FAAS: flame atomic absorption spectrometry; FIA: flow injection analysis; HPSAM: H-point standard addition method; [HPy][PF<sub>6</sub>]: 1-Hexylpyridinium hexafluorophosphate; LED: light-emitting diode based photometer for solid phase photometry; LWCC: long liquid waveguide capillary cell; MSFIA: multi-syringe flow injection analysis; USAE-SFODME: ultrasound-assisted emulsification solidified floating organic drop microextraction.

## Conclusions

A donor-active solvent-assisted liquid-phase microextraction procedure followed by spectrophotometric determination of zinc was developed. The method is based on the ion associate formation between Zn(II), thiocyanate and 2-[2-(5-dimethylamino-thiophen-2-yl)-vinyl]-1,3,3-trimethyl-3H-indolium bromide (DTVTI) reagent which is extractable by the mixtures of toluene and tributylphosphate. Considering the results, the developed procedure proved to be rapid, sensitive, efficient, reliable and easy to use for the determination of zinc.

## Supplementary information

Supplementary spectrum (<sup>1</sup>H NMR spectrum of DTVTI) is available free of charge at <http://jbc.ssbq.org.br> as PDF file.

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