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SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM WITH PYRIDOXAL SALICYLOYLHYDRAZONE

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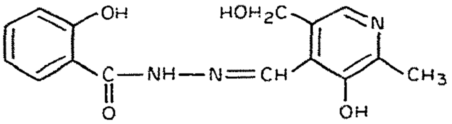
SUMMARY

The synthesis, characteristics and analytical applications of pyridoxal salicyloylhydrazone are described. The reaction between zirconium(IV) and this reagent was studied spectrophotometrically. A yellow 1:2 Zr:L complex ($\epsilon = 2.4 \times 10^4$ l mol^{-1} cm^{-1} at 395 nm) is formed from pH 3.5 to 5 M hydrochloric acid in an aqueous solution containing 2% dimethylformamide and 28% ethanol. The method is highly selective and is applied to the determination of zirconium in a steel and a nickel—chromium alloy.

The work described in this paper forms part of a systematic investigation of the use of aroylhydrazones as analytical reagents. The salicyloylhydrazone of picolinaldehyde (SHPA) has been used in the spectrophotometric determinations of nickel and zinc [1], iron(II) [2] and vanadium(V) [3]. Pyridine-2-acetaldehyde salicyloylhydrazone (PASH) has been applied for the spectrophotometric determination of vanadium(V) [4]. In this paper, the synthesis, properties and analytical applications of a new compound, pyridoxal salicyloylhydrazone (PSH) are reported. The zirconium complex is formed in 0.1—5 M hydrochloric acid, conditions under which few other complexes are completely formed. Thus, a spectrophotometric method for the determination of trace amounts of zirconium using PSH has been developed.



(PSH)

EXPERIMENTAL

Synthesis of pyridoxal salicyloylhydrazone

Dissolve 1 g of salicyloylhydrazide in 20 ml of ethanol, reflux for several minutes, and add 1.1 g of pyridoxal dissolved in 20 ml of distilled water. Reflux for 10 min, and cool to room temperature. Filter off the yellow crystals and wash with a large volume of ethanol. Dry at 110°C (yield 80%,

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m.p. 247° C). [Found: 59.6% C, 4.9% H, 14.1% N; calculated for $C_{15}H_{15}N_3O_4$: 59.8% C, 4.7% H, 13.9% N.] The reagent crystallizes with one molecule of water, but this is removed on heating between 80 and 110° C. [Found 55.3% C, 5.0% H, 13.4% N; calculated for $C_{15}H_{15}N_3O_4.H_2O$: 56.4% C, 5.3% H, 13.2% N.]

Reagents and apparatus

All solutions were prepared with analytical-reagent grade chemicals and distilled water. A 0.1% (w/v) solution of PSH was prepared by dissolving 0.1 g of reagent in 10 ml of dimethylformamide and diluting to 100 ml with ethanol.

A standard zirconium(IV) solution (2.433 g Zr l^{-1}) was prepared by dissolving zirconyl chloride (hafnium-free) in 2 M hydrochloric acid, and was standardized gravimetrically by precipitation with ammonia and ignition to ZrO_2 [5]. The other standard metal ion solutions (2—5 g l^{-1}) were prepared and standardized as described elsewhere [6]. Working solutions of the required concentration were prepared daily from the stock solutions.

Perkin-Elmer 402 and Unicam SP6-500 spectrophotometers, equipped with 1-cm glass or quartz cells, were used, as well as a Metrohm E1009 photometric titrator with a 4.0-cm glass cell. The i.r. spectra were recorded in KBr discs on a Perkin-Elmer 599 spectrometer equipped with a temperature controller for the heatable solid cell. The pH values were measured with a Beckman 3500 pH meter, equipped with a combined glass/calomel electrode.

Procedures

pK_a measurements. To the 4.0-cm glass cell (100 ml) of the photometric titrator, add 4 ml of 0.1% PSH solution, 10 ml of 0.5 M potassium chloride, 20 ml of 0.1 M hydrochloric acid and distilled water up to 100 ml. Titrate with 0.2 M sodium hydroxide. The final volume must not exceed 105 ml. Triplicate results were obtained.

Spectrophotometric determination of zirconium. To 25-ml volumetric flasks, add the sample solution containing 12—84 μg of zirconium(IV), 5 ml of 0.1% PSH solution, 2.5 ml of ethanol and 6.25 ml of 8 M hydrochloric acid, and dilute to the mark with distilled water. After 30 min, measure the absorbance at 395 nm against a blank solution prepared in the same way, but without metal ion.

Procedure for a special steel. To a 3.5-g sample, in a 50-ml Erlenmeyer flask, add 25 ml of (1 + 1) hydrochloric acid and warm gently for 30 min. Add 2 ml of 30% hydrogen peroxide, evaporate to dryness and extract the residue with 15 ml of the hydrochloric acid. Transfer the solution to a separating funnel and extract iron with ether. Remove the excess of ether on a sand bath and dilute to 50 ml with water in a 100-ml calibrated flask. Take an aliquot of 1.5 ml, add 2 ml of 1% (w/v) ascorbic acid and proceed as above for the determination of zirconium Measure the absorbance as described above.

Procedure for nickel—chromium alloy. Warm an exactly weighed amount of alloy (ca. 1.6 g) with 20 ml of aqua regia in a glass container until dissolution is complete. Remove the silica by filtration. Dilute to 100 ml in a volumetric flask with water. Percolate the solution through a Dowex 50-X8 cation-exchange column. Wash the cations onto the resin with 50 ml of 2 M hydrochloric acid. Elute the zirconium(IV) with 6 M hydrochloric acid and collect in a 100-ml volumetric flask. Take an aliquot of 2.4 ml and proceed as for special steel.

RESULTS AND DISCUSSION

Analytical properties of the reagent

The solubility of PSH was measured in various solvents. It was low (<1.2 g l^{-1}) in all solvents investigated (water, methanol, ethanol, amyl alcohol, carbon tetrachloride, chloroform, benzene and nitrobenzene), except for dimethylformamide, in which the solubility exceeded 10 g l^{-1}.

In accordance with Domiano et al. [7], selected i.r. absorption bands were assigned to stretching NH (3150 cm^{-1}), C—H (3050 cm^{-1}), C=O (1655 cm^{-1}), C=N (1550 cm^{-1}) and N—N (950—900 cm^{-1}) vibrations. The hydrate form shows a strong absorption band at 3500—3300 cm^{-1}, that may be assigned to the ν—OH vibration of the water molecule. When the i.r. spectra were recorded in the 3500—3300 cm^{-1} region at increasing temperatures (20, 60, 80, 110 and 150°C), a continuous decrease in absorbance was observed at this band; the band disappeared at 110—150°C.

The u.v. spectra of the reagent in various organic solvents are shown in Fig. 1. The spectrum in ethanol or dimethylformamide shows two main absorption maxima, at 230 nm ($\epsilon = 16.6 \times 10^3$ l mol^{-1} cm^{-1}) and 300 nm ($\epsilon = 20.9 \times 10^3$ l mol^{-1} cm^{-1}) for the former, and 320 nm ($\epsilon = 17.5 \times 10^3$ l mol^{-1} cm^{-1}) and 380 nm ($\epsilon = 17.5 \times 10^3$ l mol^{-1} cm^{-1}) for the latter. Because

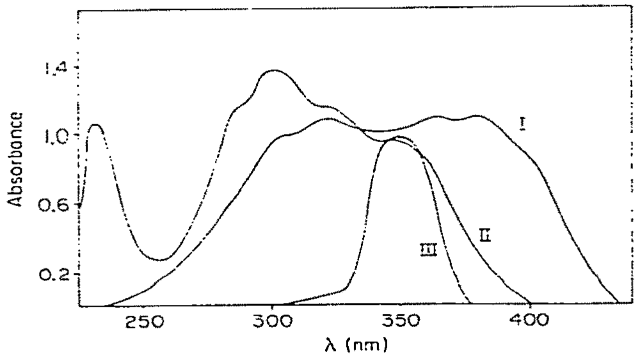

Fig. 1. Absorption spectra of 6.64×10^{-5} M PSH in (I) dimethylformamide; (II) ethanol; (III) isobutyl methyl ketone.

of the greater solubility of PSH in dimethylformamide and because absorption in the visible region was less when ethanol was used, an ethanol—dimethylformamide medium (9 + 1, v/v) was used to prepare the reagent stock solution. Solutions of 6.64 × 10^{-5} M in (9 + 1) ethanol—dimethylformamide were stable for several days.

The effect of pH on the u.v. spectra of aqueous 6.64 × 10^{-5} M solutions of the reagent (Fig. 2) shows that two main absorption bands (λ_{max} = 300 and 350 nm) are involved in acidic solution, but a bathochromic shift is produced in moderately alkaline media. The reagent showed an intense yellow colour at pH > 12, which may be due to the existence of an anion of the reagent formed by deprotonation of the —CONH— group. The reagent was stable in weakly acidic and alkaline media for several hours, but not in strong acids. The rate of hydrolysis of the C=N group increased as the pH was decreased. The hydrolysis of dilute solutions of PSH to produce salicyloyldrazide and pyridoxal in 5, 4, 3, 2, 1 and 0.1 M hydrochloric acid was complete after 7, 18, 23, 30, 60 and 240 min, respectively, at room temperature.

The ionization constants in aqueous medium at 0.05 ionic strength were determined by a simultaneous potentiometric—photometric method [8]. The average values (± standard deviation, 3 determinations) were found to be pK_1 = 4.0 ± 0.1 and pK_2 = 7.9 ± 0.1. This acid—base behaviour may be caused by protonation of the pyridine nitrogen atom (K_1) and deprotonation of the hydroxyl group (K_2).

Oxidizing agents, such as hydrogen peroxide or potassium peroxodisulphate in moderate concentration (0.2% w/v) did not perceptibly affect the absorption spectrum of PSH in aqueous—organic solutions for several hours. Reducing substances, such as hydrazine or hydroxylamine, strongly affected the reagent in alkaline media, but not in acidic media. This behaviour can be

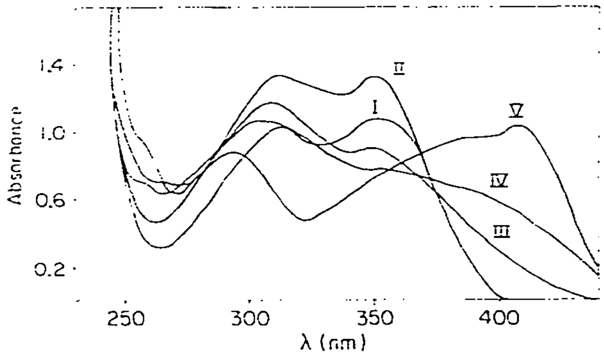

Fig. 2. Absorption spectra of 6.64 × 10^{-5} M PSH in (I) 2 M HCl; (II) pH 1.2; (III) pH 5.1; (IV) pH 7.0; (V) pH 12.1. Samples were prepared from 0.3 ml of 0.1% PSH (in 9 + 1, v/v ethanol—dimethylformamide) and appropriate amount of HCl or NaOH, and diluted to 25 ml with water.

explained by the possible formation of pyridoxal hydrazone or oxime by exchange of C=N groups [9].

A medium containing 2% dimethylformamide, 28% ethanol and 70% water was chosen for further experimental work. The main advantages are that both PSH and its complexes are soluble at the concentration used in the spectrophotometric procedures, and the reagent itself absorbs little in the spectral region in which the absorption maxima of the metal chelates are located.

The reactions of PSH with 40 cations, up to concentrations of 1 mg ml^{-1}, at pH 1.5—2 (HCl), 4.7 (acetate buffer) and 10.2 (ammonia buffer) were investigated. The spectral characteristics of the more interesting soluble complexes are shown in Table 1. Absorption maxima all appeared between 390 and 490 nm.

Study of the zirconium—PSH complex

Zirconium forms a yellow complex (Fig. 3a, λ_{max} = 405 nm at pH 1.0—3.5) which shows a hypsochromic shift as the pH decreases (λ_{max} = 395 nm at pH < 1). The complex is quickly formed. The optimum pH range for the formation of the yellow complex is from pH 3.5 to 5 M hydrochloric acid (Fig. 3b). In order to confirm that the ligand in the chelate is PSH, the reactions of zirconium with salicyloylhydrazide and pyridoxal were tested in the same way as with PSH in 0.1—5 M hydrochloric acid; neither compound formed coloured complexes with zirconium.

The stability of the chelate in several strongly acidic media was investigated. Experimental data (Fig. 4) showed that the zirconium chelate was stable in 5 or 4 M hydrochloric acid for 10—15 min, but in 3 M hydrochloric

TABLE 1

Characteristics of some soluble metal—PSH chelates in acidic media[a]

pH = 1.5—2.0 (HCl)			pH = 4.7 (acetate buffer)		
Metal ion	λ_{max} (nm)	ϵ ($\times 10^3$ l mol^{-1} cm^{-1})	Metal ion	λ_{max} (nm)	ϵ ($\times 10^3$ l mol^{-1} cm^{-1})
Cu(II)	420	15.8	Cu(II)	390	17.4
Mo(VI)	420	2.4	Fe(II)	420, 490	12.6, 7.0
V(V)	410	4.6	U(VI)	425	6.0
Zr(IV)	405	27.4	Ti(IV)	450	1.8
U(VI)	390	3.0	Al(III)	425	29.7
Ti(IV)	390, 440	5.9, 3.6	Ga(III)	425	10.4
Al(III)	420	20.3	Ni(II)	425	22.0
Ga(III)	420	2.8	Co(II)	420	13.3
			Zn(II)	425	9.8

[a] In a solution containing 2% dimethylformamide and 28% ethanol (v/v). All complexes were yellow or orange.

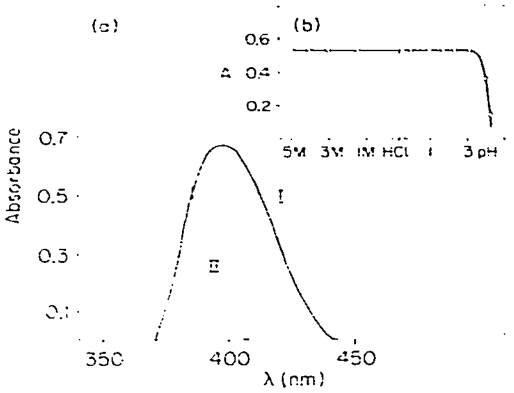

Fig. 3. (a) Absorption spectra in 2 M HCl of (I) Zr—PSH complex (2.4 μg Zr ml^{-1}); (II) reagent blank. (b) Absorbance vs. pH plot for the Zr—PSH complex: 1.92 μg Zr ml^{-1}, 395 nm. All solutions contain 2% dimethylformamide and 28% ethanol (v/v).

acid it was stable for 1 h. The complex was stable for several days in 2, 1 or 0.1 M hydrochloric acid, after a 30-, 20-, or 15-min reaction time, respectively. Chelation stabilizes the C=N bond, so that the chelate is more stable than the free ligand at the same concentration of hydrochloric acid.

The stoicheiometry of the zirconium complex was evaluated by the continuous variations [10, 11] and mole ratio [12] methods. Both gave a metal:ligand ratio of 1:2. From the data obtained by the continuous variations method, the apparent stability constant in 2 M hydrochloric acid was calculated to be $\beta_2 = 7.96 \times 10^9$ l^2 mol^{-2}.

The electrical charge of the complex was studied by means of ion-exchange resins. The yellow complex in 2 M hydrochloric acid was retained by Dowex 50-X8 (hydrogen form) but not by Dowex 1-X8 (chloride form). Therefore, under these experimental conditions the complex carried an overall positive charge.

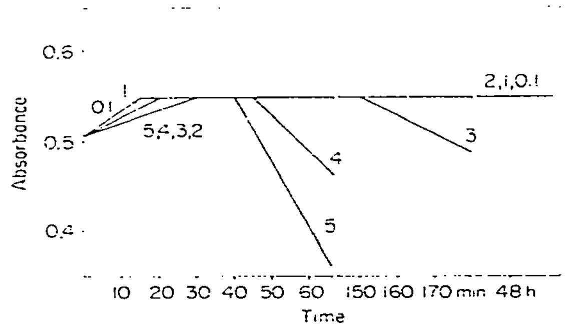

Fig. 4. Variation of the absorbance of the zirconium complex in strongly acidic media (395 nm, 1.92 μg Zr ml^{-1}). Numbers correspond to molarity of HCl.

Spectrophotometric determination of zirconium

Beer's law was obeyed between 0.48 and 3.4 μg Zr ml^{-1} (absorbance between 0.152 and 0.917); the molar absorptivity at 395 nm was 2.40 × 10^4 l mol^{-1} cm^{-1}. The Ringbom plot showed that the optimum range for accurate determinations was 0.6—2.8 μg Zr ml^{-1}. The Sandell sensitivity was 3.8 ng cm^{-2}. The precision of the method was checked by measuring the absorbance of eleven separate samples each containing 1.44 μg Zr ml^{-1}; the relative error ($P = 0.05$) was ±0.30%.

Foreign ions (54 diverse ions) for interference tests were added as their chlorides or nitrates (for cations) or their sodium or potassium salts (for anions). For the determination of 36 μg of zirconium(IV) in 25 ml of solution, the ions were added up to a maximum of 25 mg. The tolerance limit was taken as the amount which caused an error of not more than 3% in the recovery of zirconium. The results are given in Table 2. Ascorbic acid did not interfere at the 1.2 mg ml^{-1} level; 5 μg ml^{-1} of iodate, bromate or EDTA gave errors of 7, 35 and 13%, respectively. Cerium(IV), copper(II), iron(III) and vanadium(V) did not interfere in the presence of 1.2 mg ml^{-1} ascorbic acid at 100, 75 and 75 μg ml^{-1}, respectively.

Determination of zirconium in alloys. The method was satisfactorily applied to the determination of zirconium in two standard samples, a steel (BCS 458) and a chromium—nickel alloy (BAM 326/1-204). Iron was partially separated by extraction with ether, in the analysis of steel [13]; in order to prevent interference from iron(III) and vanadium(V), ascorbic acid

TABLE 2

Effect of foreign ions on the determination of 36 μg of zirconium per 25 ml by the recommended method

Foreign ion	Tolerance limit (mg per 25 ml)
Tl(I), Ba, Mg, Be, Sr, Pb, Zn, Co(II), Mn(II), Al, Sb(III), Sn(IV), Se(IV), As(V), U(VI), Ag[a], ClO_4^-, SCN^-, NO_3^-, $B_4O_7^{2-}$, CO_3^{2-}, SO_3^{2-}, $S_2O_8^{2-}$, tartrate, citrate	25
Ga(III)	19
Mo(VI), Cd[b], Ti(IV), Bi(III), Ni	13
As(III), Li[b], Cd	6
Ce(IV)[c], Pd(II), Sn(II), W(VI), Ca, $C_2O_4^{2-}$	2.5
Fe(II), Fe(III)[c], Cu(II)[c], Hg(II), I^{-}[b], IO_3^-	1.9
V(V)[c], Pt(IV)[b], I^-	1.3
Cr(III), Hg(I), Pt(IV)	0.6
Ce(IV), Th	0.25
Fe(III), Cu(II), PO_4^{3-}, F^-	0.13

[a] Sample centrifuged prior to absorbance measurement. [b] Measured at 400 nm. [c] With addition of 3 ml of 1% (w/v) ascorbic acid.

was added to solutions. Chromium and nickel were separated by cation-exchange during the analysis of the alloy [14, 15]. Five separate determinations were done in both instances. The reported zirconium values for the steel and alloy are 0.045% and 0.129%, respectively; the values found (± standard deviations) were (0.046 ± 0.001)% and (0.125 ± 0.002)%, respectively.

Critical comparison of PSH, SHPA and PASH as analytical reagents

PSH possesses the chromogenic grouping (OH)C=C—CO—NH—N=C=C(OH) and may function as a bidentate or tridentate ligand. SHPA and PASH have similar structures, —(OH)C=C—CO—NH—N=C—C=N—, differing in the aldehyde or ketone condensed to the hydrazine chain. Comparison of their analytical behaviour is therefore of interest.

The preparation of the three reagents is easy and a relatively high yield is obtained. The absorption spectra of the reagents and their variation with pH are similar.

The qualitative reactions of metal ions with PSH and SHPA (derived from aldehydes) are similar, but those with PASH (derived from a ketone) are not. Possibly the methyl group on the ketone affects complex formation, because of steric hindrance. However, the reactivity of the three reagents in strongly acidic media is different; PSH is more resistant to hydrolysis of the C=N group than the other ligands. This may be due to intramolecular hydrogen bonding between a nitrogen atom of the hydrazide residue and the hydroxyl group on the pyridine ring, so that a six-membered ring is produced.

The most selective reactions for PSH were with zirconium(IV) (2 M hydrochloric acid, λ_{max} = 395 nm), titanium(IV) (pH 0.9—2.5, λ_{max} = 390 nm, shoulder at 440—450 nm) and aluminium(III) (pH 1.8—3.1, λ_{max} = 400 and 420 nm, and pH 4.2—6.0, λ_{max} = 425 nm). SHPA and PASH gave the most selective reactions with vanadium(V) and iron(II) in aqueous media at optimum pH values of 2.5—4.0 (V—SHPA, λ_{max} = 400 nm), 6.0—8.0 (Fe—SHPA, λ_{max} = 380 and 620 nm), 3.5—6.0 (V—PASH, λ_{max} = 386 nm) and 6.5—8.0 (Fe—PASH, λ_{max} = 378 and 640 nm). Nevertheless, it is necessary to extract the metal chelates of PASH and SHPA in order to avoid precipitation and to obtain high selectivity. It is evident that the position of the nitrogen atom of the pyridine ring has an effect on complex formation. The green iron(II)—PSH complex is not formed because PSH does not possess the ferroine grouping, unlike the other ligands. PASH and SHPA form with zirconium(IV) a soluble yellow complex, but have unfavourable maximum wavelengths (355 and 370 nm, respectively) and provide less sensitivity than the Zr—PSH complex.

PSH has the advantages that spectrophotometric determinations may be made in aqueous media and in strongly acidic conditions. Also most metal chelates of PSH have absorption maxima at longer wavelengths than those of SHPA and PASH.

TABLE 3

Comparison of reagents for the spectrophotometric determination of zirconium

Compound	Optimum pH	λ_{max} (nm)	ϵ ($\times 10^3$ l mol^{-1} cm^{-1})	Interferences	Ref.
Arsenazo-III	9 M HCl	665	120[a]	Th, U(IV), F^-, $C_2O_4^{2-}$	16
Alizarin red S	0.1–0.2 M HCl[b]	520	7	F^-, PO_4^{3-}, SiO_3^{2-}, Mo(VI), Sb(III), W(VI)	17
Pyrocatechol violet	5.2[c]	530–550	25	F^-, Sb(III), Sn(IV)	16
Xylenol orange	0.5–1 M $HClO_4$	535	35	F^-, PO_4^{3-}, $C_2O_4^{2-}$	16
Picraminazo H	0.1 -1.0 M HCl	619	14	Hf, Cu(II), EDTA, F^-	18
Quercetin	0.1–1.0 M HCl	440	31	Sn(IV), Cr(VI), Mo(VI), W(VI), Sb(III), Nb, Ta, Hf, F^-, PO_4^{3-}, AsO_4^{3-}, $C_2O_4^{2-}$	19
Chrome azurol S	1.4	555	48	Fe(III), PO_4^{3-}, $C_2O_4^{2-}$, citrate, H_2O_2, EDTA	20
Stilbazo	3	585	56	Hf, Be, In, Mn(II), Mo(VI), Ti, Th, W(VI), V(IV, V), PO_4^{3-}, $C_2O_4^{2-}$, citrate, EDTA	21
Solochrome azurine BS	4.5–5.5	545	11	Th, F^-, $C_2O_4^{2-}$, PO_4^{3-}	22
Robinetin	2.5 M HCl	415	20	Cu(II), Fe(II), Ce(IV), F^- Mo(VI), IO_3^-	23
Gallein	2.3	530	8	Th, Ce(IV), Tl, Fe, W(VI), U(VI), halides, SO_4^{2-}	24
Pyridoxal salicyloylhydrazone	0.1–5 M HCl	395–400	24	—	—

[a] Sensitivity is very dependent on acidity. [b] In presence of gum arabic. [c] In presence of EDTA.

Zirconium was selected for further study because the Zr—PSH complex is formed in 0.1—5 M hydrochloric acid; in 0.1—2 M hydrochloric acid, the complex persists for several days, conditions under which few other complexes are completely formed. Further, the spectrophotometric determination of zirconium with PSH is more sensitive and selective than the other procedures (Table 3). The shorter wavelength of absorbance measurements in the PSH method with respect to the other procedures is compensated by the very low reagent blank.

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