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Derivative Spectrophotometric Determination of Trace Manganese after Separation and Preconcentration with the Ion Pair of 2-(5-Bromo-2-pyridylazo)-5-diethylaminophenol and Ammonium Tetraphenylborate

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Manganese is quantitatively retained on 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP)-ammonium tetraphenylborate with microcrystalline naphthalene or by a column method in the pH range 7.5–10.5 from a large volume of aqueous solutions of various samples. After filtration, the solid mass consisting of the manganese complex and naphthalene was dissolved with 5 mL of dimethylformamide and the metal was determined by third derivative spectrophotometry. Manganese complex can alternatively be quantitatively adsorbed on ammonium tetraphenylborate-naphthalene adsorbent packed in a column and determined similarly. About 0.1 μg of manganese can be concentrated in a column from 500 mL of aqueous sample, where its concentration is as low as 0.2 ng/mL. The interference of a large number of anions and cations has been studied and the optimized conditions developed were utilized for the trace determination of manganese in various samples.

Key words: Trace manganese determination; derivative spectrophotometry; (5-Br-PADAP)-(TPB)-naphthalene

INTRODUCTION

Manganese toxicity is characterized by a severe psychiatric disturbance, which can induce memory impairment, disorientation, hallucinations, speech disturbance, compulsive behaviour and acute anxiety. The World Health Organization study group suggested an occupational limit of manganese in air as 0.3 mg/m^3 and in water as 0.3 ppm[1]. Very low concentrations of manganese are present in various complex samples like alloys, plants, sea-water etc. Therefore, it is very important from the analytical point of view to develop sensitive, selective, rapid and economical methods for its quantitative determination even when present in trace amounts. Graphite furnace atomic absorption spectroscopy, neutron activation analysis, inductively coupled plasma-atomic emission spectroscopy, inductively coupled plasma-mass spectrometry and direct current plasma atomic emission spectrometry may be used for the determination of metals at trace level[2–7] but these instruments are expensive, day-to-day maintenance is high and they are not free from various types of inherent interferences[2–6, 8]. A survey of the literature reveals that manganese may be determined spectrophotometrically using various complexing agents[7, 9–14] but many of them have limited sensitivity, preconcentration factor and selectivity as compared to the present method.

Derivative spectrophotometry offers the advantages of increased selectivity and sensitivity compared with normal spectrophotometry[15–22]. Spectrophotometers equipped with suitable derivative units enable not only the derivative spectra of the first and second orders to be obtained but also higher orders.

The increased selectivity in derivative spectrophotometry results from the fact that bands which overlap in normal absorption spectra appear as separated bands in the derivative spectra. Derivative spectrophotometry can increase sensitivity owing to the amplification of derivative signals and lowering of noise; improvements in selectivity and sensitivity are easier to obtain in instances where the bands in the normal absorption spectra are fairly sharp[23, 24].

Sodium tetraphenylborate (TPB) and its derivatives have been used in the estimation of alkali and univalent metal ions[25–27]. It has also been used as a counter ion in the extraction and adsorption of some metal complexes into molten naphthalene[28–30] and microcrystalline naphthalene respectively[31–33]. A survey of the literature reveals that metal ions may be preconcentrated on various adsorbents such as thiol cotton[34], silanized glass beads[35], silica gel[36], Amberlite XAD-4 resin[37], cellulose[38], green tea leaves[39] and polythioether foams[40]. Some of these adsorbents may be fairly effective for preconcentration of metal ions, but their methods of preparation are lengthy and involve rigid control of conditions. The desorption of the metal is carried out by the slow process of elution (the metal complex is probably held by the interior surfaces of the adsorbent and thus the adsorbed complex is not eluted easily); hence the procedure is time-consuming. Solvent extraction is a simple and convenient technique for separating and concentrating metal ions, but it cannot be applied directly to metal ions which form stable complex with the chelating agents only at elevated temperature. This difficulty can be overcome by using naphthalene as the extractant[41] for thermally stable metal chelates[42]. Solid-liquid separation after adsorption of metal chelates on microcrystalline naphthalene is more rapid and convenient and can be applied to many types of metal complexes[31, 32]. The preconcentration of manganese ion is also possible by passing its aqueous solution over naphthalene-NH_4-TPB adsorbent taken in a column. The microcrystalline naphthalene method is rapid but the column method gives a better preconcentration factor[20–22].

In this paper, a highly selective and sensitive preconcentration method has been developed, that uses 2-(5-bromo-2-pyridylazo)-5-diethylaminophenol (5-Br-PADAP) as the complexing reagent in addition to the (NH_4^+) (TPB^-) ion pair supported on naphthalene. The 5-Br-PADAP and its derivatives are highly selective for manganese. The 5-Br-PADAP reacts with manganese to form a water-soluble complex cation, but in the presence of the TPB anion it forms a water-insoluble complex (Mn-5-Br-PADAP-TPB). Preliminary observations revealed that the Mn-5-Br-PADAP complex cation could be quantitatively retained on an ammonium tetraphenylborate adsorbent supported on naphthalene. The solid mass, consisting of the metal ion associated complex and naphthalene, can easily be dissolved with a suitable organic solvent such as dimethylformamide (DMF) and the manganese is determined by third derivative spectrophotometry. The interference of a number of metal ions and anions on the estimation of manganese has been studied in detail and the developed method is found to be highly sensitive and selective and has been employed for the estimation of manganese in complex materials.

EXPERIMENTAL

A Shimadzu UV 160 spectrophotometer with 1.0 cm quartz cell was used. A Beckman pH meter was employed for pH measurements. A funnel-tipped glass tube (60 mm × 6 mm) was used as a column for preconcentration. It was plugged with polypropylene fibres and then filled with the adsorbent to a height of 1.0–1.2 cm after pressing lightly with a flat glass rod. All glassware was washed with a mixture of concentrated sulfuric and nitric acids (1 + 1) before use.

All reagents were of analytical reagent grade. A standard manganese solution was prepared from manganese(II) sulfate in distilled water and standardized by known methods[43]. A 0.01% solution of 5-Br-PADAP in ethanol was prepared. Buffer solutions of pH 3–6, 6–8 and 8–11 were prepared by mixing appropriate ratios of a 0.5 M acetic acid and 0.5 M sodium acetate solution, 0.1 M sodium dihydrogen phosphate solution and 0.1 M dipotassium hydrogen phosphate solution, and 0.5 M ammonia solution and 0.5 M ammonium acetate solution, respectively. A 1% solution of sodium tetraphenylborate (TPB) was prepared in distilled water. A 20% solution of naphthalene was prepared in acetone. Solutions of alkali metal salts (1%) and various metal salts (0.1%) were used for studying the interference of anions and cations respectively.

Preparation of naphthalene-NH_4-TPB adsorbent

A solution of naphthalene was prepared by dissolving 20 g of naphthalene in 40 mL of acetone on a hot-plate stirrer at 30–35°C. This solution was transferred into 1500 mL of distilled water containing 25 mL of 1 mol L^{-1} ammonium acetate and 75 mL of 1 mol L^{-1} ammonia solution (pH 9.5), in a fast stream continuous flow with continuous stirring at room temperature. Then, to this solution, 500 mL of an aqueous solution containing 1.7 g of TPB was added. The naphthalene coprecipitated with NH_4^+ and TPB^-. The solution was stirred for about 2 h and then allowed to stand for 2 h. The supernatant solution was decanted off and the remaining solid mass was washed twice with distilled water. The adsorbent in the form of a slurry was stored in a bottle for subsequent use.

General procedure for the column method

Sample solution (up to 500 mL) containing 0.1–15 μg of manganese was taken in a beaker and 2.0 mL of 0.01% alcoholic solution of 5-Br-PADAP and 2.0 mL of buffer of pH 8.5 were added to it. The column loaded with the adsorbent NH_4-TPB-naphthalene was conditioned to pH 8.5 by passing 2–5 mL of the buffer solution at a flow rate of 1 mL min^{-1}. The manganese sample solution prepared above was then passed at a flow rate of 1 mL min^{-1}. The packing in the column was washed with a few millilitres of distilled water and then aspirated strongly for 2–3 min, pushing down the solid mass in the column with a glass rod in order to eliminate the excess water attached to the adsorbent. The metal complex was dissolved out of the colunm along with naphthalene with 5 mL of DMF. The third derivative absorption spectra in the range 500–650 nm were recorded against a blank solution prepared in the same way. The signal was measured between $\lambda_1 = 604$ nm and $\lambda_2 = 575$ nm A calibration curve was prepared by taking various known amounts of manganese under the conditions given above.

General procedure for microcrystalline naphthalene: Sample solution (up to 200 mL) containing 0.1–15 μg of manganese solution was placed in an Erlenmeyer flask with tightly fitting stopper. Then 2 mL of 0.01% of the reagent (5-Br-PADAP) was added to it. The pH was adjusted to 8.5 with 2 mL of the buffer, and then 2 mL of 1% TPB solution was added. The solution was mixed well and allowed to stand for a few seconds. Then, 2 mL of a 2% solution of naphthalene in acetone was added to it with continuous shaking. The solid mass so formed consisting of naphthalene and metal complex was separated by filtration on a Whatman filter paper (No. 1041). The residue was dried in the folds of a filter paper and transferred to the Erlenmeyer flask. The solid mass consisting of the metal complex along with naphthalene was dissolved in 5 mL of dimethylformamide. Finally, the third derivative absorption spectrum was recorded in the range 500–650 nm against a blank solution prepared in the same way.

RESULTS AND DISCUSSION

Spectrophotometric measurements: The zero order (normal spectrophotometric) and third order derivative spectra of the complex are shown in Fig. 1. As can be seen, the higher wavelength peaks of the third derivative spectra are more

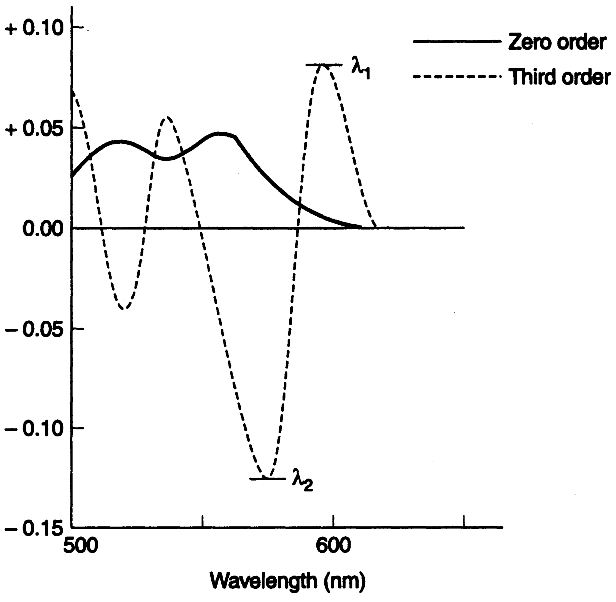

Fig. 1. Zero and third order spectrum of the naphthalene-Mn-(5-Br-PADAP)-TPB complex. (Mn, 1.5 μg; buffer, 2 mL; pH, 8.5; 5-Br-PADAP, 2.0 mL (0.01%); solvent, 5 mL DMF; reference, reagent blank.

significant. The sensitivity of the third order derivative is much higher than for zero (normal), first and second orders. Third derivatization manganese gives sharper zero order bands (normal spectrophotometric bands) and gives higher signals on the resulting spectra. The characteristics of derivative spectra, such as peak height and noise level, depend on the choice of parameters such as order of derivative, scan speed and integration time during recording of the spectra. The optimum parameters were chosen from preliminary experiments. The best results were obtained from third derivative spectra due to high signals at $\lambda_1 = 604$ nm and $\lambda_2 = 575$ nm, with a length interval of 9 nm. Manganese could be determined by measuring the signal between the baseline and the corresponding peaks. It could also be determined from the signal between λ_1 and λ_2. In the present work, a peak-to-peak method between λ_1 and λ_2 was applied.

Retention characteristics of NH_4-TPB: Sodium tetraphenylborate (TPB) is soluble in water; it forms water-insoluble precipitates with some alkali metal ions such as K^+, Rb^+, Cs^+ (but not Li^+, Na^+), and univalent metal ions such as Ag^+, Tl^+, and Cu^+ , but does not form precipitates with multivalent metal ions. It has been used as a gravimetric and volumetric reagent. Furthermore, it also reacts with ammonium salts such as NH_4^+ and its derivatives to form water-insoluble precipitates. The TPB^- forms a weakly bonded ion pair with NH_4^+ in aqueous solution and coprecipitates with microcrystalline naphthalene as follows:

$$NH_4^+ + TPB^- \longleftrightarrow (NH_4^+)(TPB^-)(s)$$

From the experimental observation, the NH_4-TPB ion-pair, produced from TPB^- and ammonium acetate in aqueous solution, when supported on naphthalene, was unstable and partly desorbed from the surface of the naphthalene in the column on passage of the buffer of pH 5.5. However, the NH_4-TPB ion-pair prepared in acetate buffer of pH 9.5 is highly stable and TPB^- is not desorbed even on washing with water or the buffer of pH 8.5. The adsorbent shows excellent absorption characteristics for various cationic metal complexes such as $Fe(1,10\text{-Phen})_3^{2+}$. In this work, TPB^- has been selected as the counter-ion because of its purity and moderate price.

Reaction conditions: These were established with the use of 1.5 μg manganese. The adsorption of manganese on this adsorbent was found to be maximum in the pH range 7.5–10.5. In subsequent studies, the pH was maintained at approximately 8.5. Addition of 0.5–5 mL of the buffer did not affect the retention of manganese and the use of 2 mL is recommended. Various amounts of 0.01% alcoholic solution of 5-Br-PADAP were tried. Manganese was quantitatively adsorbed on the adsorbent over the range 0.5–3.0 mL of the reagent. Therefore, 2.0 mL of the reagent is recommended in the present study.

Various amounts of naphthalene (20% solution of naphthalene in acetone) were added to the sample solutions keeping other variables constant. It was observed that the signal height remained constant with the addition of 1.0–4.0 mL of 20% naphthalene solution. Therefore 2.0 mL of 20% naphthalene solution was used in subsequent studies. The effect of shaking time on the adsorption indicated that the signal height remained constant over a range of 0.5–5.0 min. Therefore, 1.0 min of shaking time was maintained in the present work.

In the case of column method, the flow rate was varied from 0.2 to 8 mL/min.

It was found that a flow rate of 0.2–5.0 mL/min did not affect adsorption. A flow rate of 1 mL/min was recommended in all experiments.

The volume of the aqueous phase was varied in the range of 10-700 mL under the optimum conditions, keeping other variables constant. It was observed that the signal height was almost constant up to 200 mL (preconcentration factor of 40). However, for convenience, all the experiments were carried out with 40 mL of the aqueous phase, whereas, in the case of column method, signal height was almost constant up to an aqueous phase volume of 500 mL. Therefore, a preconcentration factor of 100 can be achieved by the column.

Choice of solvent: A number of solvents were tried to dissolve the metal complex along with naphthalene. Since the solid mass is dissolved in a small volume (3–5 mL) of solvent, it is essential to select a solvent in which the chelate is highly soluble and also sensitive for UV-Vis spectrophotometric measurements. The solid material is insoluble in ordinary organic solvents such as toluene, 1,2-dichloroethane, n-hexane, nitrobenzene, isoamyl alcohol, n-amyl alcohol, ethyl acetate, methyl isobutyl ketone, chloroform and dioxane, but soluble in dimethyl sulfoxide, dimethylformamide and propylene carbonate. Dimethylformamide was preferred because of the high solubility and stability of metal complex on naphthalene. It was found that 2–3 mL of this solvent was sufficient to dissolve the entire mixture, thus further enhancing the sensitivity of the method. Since only a small volume (3–5 mL) of the solvent is required to dissolve the solid mass, it was essential to study the effect of the surplus water attached to the absorbent. It was found that the surplus water caused the absorbance to decrease by 10–12% and led to an error in the determination. Thus, it was necessary to eliminate the water attached to naphthalene in the column completely by aspirating the column for 2–3 min.

Retention capacity of the adsorbent: The retention capacity of the adsorbent was determined by a batch method. The experiment was performed by adding 500 μg of manganese, 2 mL of the buffer (pH 8.5), a suitable amount of reagent 5-Br-PADAP and 40 mL of water in a beaker. This solution was transferred into a separatory funnel and then a suitable amount of the adsorbent naphthalene-NH_4-TPB added to it. The separatory funnel was vigorously shaken on a mechanical shaker for 5 min. The solid mass was separated by filtration and manganese was determined from the filtrate. The solid mass on the filter paper was dried in an oven, kept in a desiccator, and then weighed to determine the mass of the adsorbent. The maximum amount of manganese retained was 7.0 mg/g of the adsorbent.

Calibration, sensitivity, precision and stability: Considering that it is possible to retain 25 ng of manganese from 500 mL of solution passing through the column, the dissolution with 5 mL DMF gives a detection limit of 50 pg/mL for manganese at the minimum instrumental settings. The linearity was maintained in the concentration range of 0.2 ng/mL to 1.0 μg/mL manganese in aqueous solution or 0.02 to 3.0 μg/mL manganese in final DMF solution with a correlation factor of 0.9999. Eight replicate determinations of 1.5 μg of manganese in 5 mL DMF solution gave a mean intensity in the third derivative spectrum, measured from the peak-to-peak signal between λ_1 and λ_2, of 0.197 with a relative standard deviation of ±1.1%. The sensitivity was 0.668 (d^3A/dnm^3)

mL/μg from the slope of the calibration curve. The solution was stable for over 7 days.

Effect of foreign ions: Various salts and metal ions were added individually to a solution containing 1.5 μg of manganese and the general procedure was applied. The tolerance limit (error < 3%) is given in Table-1. Among the salts examined, most did not interfere at the g-mg level; only EDTA interfered seriously due to the higher formation constant of this metal-EDTA complex than that of 5-Br-PADAP. Among the metal ions studied, many did not interfere even at the milligram level. Thus the method is highly selective without the use of masking agents. The proposed procedure has therefore been applied to the determination of manganese in alloys and biological samples without any prior separations.

Analysis of manganese in standard alloys: The proposed method was applied to the determination of manganese in Nippo Keikinzoku Kogyo (NNK) CRM 916, No. 920 Aluminum Alloy, NKK No. 1021, Al, Si, Cu, Zn Alloy, Japanese Standards of Iron and Steel (JSS) CRM 651-7 and 653-7 Stainless Steel. A 0.1 g sample of the standard aluminium alloy or steel was completely dissolved in 6–14 mL of hydrochloric acid (1 + 1) by heating on a water-bath and then 1 mL of 30% (v/v) hydrogen peroxide was added to it. The excess of peroxide was decomposed by heating the sample on a water-bath. The solution was cooled, filtered if needed and diluted to 100 mL with distilled water in a standard flask. An aliquot of this sample was taken and the general procedure was applied. The results obtained are given in Table-2. These results are in agreement with the certified values.

TABLE-1
EFFECT OF FOREIGN SALTS AND IONS

Salt or ion	Tolerance limit
$CH_3COONa\cdot 3H_2O$, NaCl, KNO_3	1 g
NH_4Br, $(NH_4)_2SO_4$	350 mg
K_2CO_3	150 mg
Sodium potassium tartrate	85 mg
Potassium thiocyanate	65 mg
Trisodium citrate, sodium oxalate	45 mg
Na_2EDTA	85 μg
Zn(II), Cd(II)	25 mg
Pb(II), Fe(III)	20 mg
Cr(III), Al(III)	17 mg
Ti(VI), Se(VI), Ga(III)	10 mg
Ni(II), Cu(II), Co(II), Sb(III)	9.5 mg
U(VI), V(V), Te(IV), Sn(II)	8.5 mg
Rh(III), Ru(III), Mo(VI)	6.0 mg
Pd(II), Os(VIII)	4.5 mg

TABLE-2
ANALYSIS OF MANGANESE IN STANDARD ALLOYS

Sample	Composition (%)	Found*
JSS 651-7 Stainless steel	C, 0.047; Si, 0.072; N, 0.0312; P, 0.028; Cr, 18.60; Al, 0.002; S, 0.0063; Mo. 0.84; Co, 0.22; Mn, 1.72; Ni, 9.20; Cu, 0.082	1.70 ± 0.05[a]
JSS 653-7 Stainless steel	C, 0.068; Si, 0.63; N, 0.0276; Cr, 22.53; Co, 0.35; Mn, 1.72; Ni, 13.91; Cu, 0.030	1.75 ± 0.04[b]
NKK No.916 Aluminium alloy	Si, 0.41; C, 0.41; Fe, 0.54; Mg, 0.10; Cr, 0.05; Sn, 0.05; Zn, 0.30; Ti, 0.10; Pb, 0.04; Sb, 0.01; B, 0.0006; Zr, 0.05; Co, 0.03; Mn, 0.11; Bi, 0.03; Ni, 0.06; V, 0.02; Cu, 0.27	0.12 ± 0.01[a]
NKK No. 1021 Al, Si, Cu. Zn alloy	Pb, 0.18; Zn, 1.76; Si, 5.56; Sn, 0.10; Mg, 0.29; Ti, 0.04; Cr, 0.03; Fe, 0.99; Bi, 0.01; Zr, 0.01; Sb, 0.01; Ca, 0.004; Mn, 0.20; Ni, 0.14; V, 0.007; Cu, 2.72	0.21 ± 0.01[b]
NKK No. 920 Aluminium alloy	Cr, 0.27; Si, 0.78; Bi, 0.06; Ti, 0.15; Sn, 0.20; Ga, 0.05; Pb, 0.10; Fr, 0.72; Zn, 0.80; Ca, 0.03; Mg, 0.46; Sb, 0.10; Co, 0.10; Mn, 0.20; Ni, 0.29; V, 0.15; Cu, 0.71	0.194 ± 0.007[a]

*Average of five determinations ± standard deviation.
[a] Column method was applied.
[b] Microcrystalline naphthalene method was applied.

Analysis of manganese in biological samples: The accuracy and applicability of the proposed method has been applied to the determination of manganese in National Institute for Environmental Studies (NIES, No. 1 Pepperbush; NIES, No. 3 Chlorella; NIES, No. 5 Human Hair and NIES, No. 7 Tea Leaves). A 0.1 g sample was taken in a beaker and dissolved in concentrated nitric acid (*ca.* 5 mL) with heating. The solution was cooled, diluted and filtered. The filtrate was made to 100 mL with water in a calibrated flask. An aliquot of the sample solution was taken individually and manganese was determined by the general procedure. The results are given in Table-3 which are in good agreement with the certified values.

Conclusion

A solid ion-pair compound produced from NH_4^+ and TPB^- naphthalene provides a simple and economical method for the preconcentration of manganese from large volumes of alloys and biological samples using 5-Br-PADAP as the complexing agent. This reagent is fairly sensitive and selective for manganese but, with the preconcentration step and the use of derivative spectrophotometry, its sensitivity and selectivity have been further improved. Thus the developed method can be used safely for the estimation of manganese in a number of complex materials. Since the adsorbent provides TBP^- as the counter anion, the adsorbent may therefore be used for the preconcentration of various types of cationic metal complexes. Although, the metal may be estimated by atomic absorption spectrophotometry after the preconcentration step. Atomic absorption spectrophotometry is a relatively expensive instrument, and day-to-day expenses and maintenance are high. Another, cheaper, technique is differential pulse polarography which could be tried for the estimation of manganese after the preconcentration step. As a whole, the proposed method is highly sensitive, selective, simple and highly economical (it requires simple glassware and a small volume of the organic solvent to dissolve the solid mass from the column) for the estimation of manganese.

TABLE-3
ANALYSIS OF MANGANESE IN BIOLOGICAL SAMPLES

Sample	Composition	Found*†
NIES, No. 1 Pepperbush	K, 1.51 ± 0.06; Mn, 0.203 ± 0.107; Mg, 0.408 ± 0.020; Ca, 1.38 ± 0.07; Cd, 6.7 ± 0.5; Ni, 8.7 ± 0.6; Fe, 205 ± 17; Co, 23 ± 3; Pb, 5.5 ± 0.8; Cu, 12 ± 1; Zn, 340 ± 20; Ba, 165 ± 10; Na, 106 ± 13; Rb, 75 ± 4; Sr, 36 ± 4; As, 2.3 ± 0.3; P, (1100); Cr (1.3); Cs, (1.2); Tl, (0.13); Hg, (0.056) μg/g	0.200 ± 0.007[a]
NIES, No. 3 Chlorella	K, 1.24 ± 0.06; Mg, 0.33 ± 0.02; Ca, 0.46 ± 0.03; Fe, 0.185 ± 0.010; P (1.7)% ; Zn, 20.5 ± 1.0; Sr, 40 ± 3; Co, 0.87 ± 0.05; Cd, (0.026); Mn, 69 ± 5; Pb, (0.60); Cu, 3.5 ± 0.3; Sc, (0.013) μg/g	67 ± 2[b]
NIES, No. 5 Human Hair	Pb, 6.0; Cd, 0.20; K, 34; Rb, 0.19; Sb, 0.07; Zn, 169; Al, 240; Fe, 225; Mg, 208; Hg, 4.4; Sc, 0.05; Se, 1.4; Na, 26; Sr, 2.3; Ti, 3.2; Ca, 728; Cr, 1.4; Ba, 2.2; Co, 0.10; Mn, 5.2; Cu, 16.3; Ni, 1.8 μg/g	5.13 ± 0.09[a]
NIES, No. 7 Tea leaves	Pb, 0.80; Cd, 0.030; Sb, 0.014; Zn, 33; Cr, 0.15; Al, 775; Mg, 1530; Ba, 5.7; K, 18600; Sc, 0.011; Na, 15.5; Sr, 3.7; Ca, 3200; Cs, 0.22; Co, 0.12; Mn, 7.00; Ni, 6.5; Cu, 7.0 μg/g	6.9 ± 0.1[b]

*Average of five determinations.
± Standard deviation.
†Standard addition method was applied.
NIES: National Institute of Environmental Studies reference materials.
NIES No. 1 and No. 3: Values in parentheses were approximate and not certified.
[a]Column method was applied.
[b]Microcrystalline naphthalene method was applied.

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