

Solvent extraction of manganese (VII) with a new analytical reagent

D. Kostova*,

M. Kamburova

Agricultural University – Plovdiv,
Laboratory Complex,
12, Mendeleev Str.,
4000 Plovdiv, Bulgaria

The optimum conditions for the spectrophotometric determination of manganese (VII) as an ion-association complex with triphenylmethane dye Crystal Violet (CV) by liquid–liquid extraction are presented. Crystal Violet was proposed as a new reagent for the spectrophotometric determination of micro amounts of manganese (VII). The ratio MnO_4^- : CV^+ is 1 : 1. In acidic conditions, manganese (VII) forms a blue complex with CV, which can be extracted with 1,2-dichloroethane with an absorption maximum at 250 nm. Beer's law is obeyed in the range of 0.2–2.2 $\mu\text{g ml}^{-1}$ manganese (VII). The molar absorptivity of the ion-pair is $1.54 \cdot 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$, and Sandell's sensitivity is $3.57 \cdot 10^{-3} \mu\text{g cm}^{-2}$. The interferences of different cations and anions on manganese determination were also investigated. The proposed new method is extremely sensitive, rapid, reproducible and has been satisfactorily applied for the determination of trace amounts of manganese in plants.

Key words: manganese determination, crystal violet, solvent extraction, spectrophotometry, plants

INTRODUCTION

Studies of changes in the content of microelements are of particular interest. Manganese is one of the microelements that are actively absorbed by plants. The formation of plant mass depends on manganese supply. Manganese is important for the synthesis of organic substance in plants and for the metabolism of a number of nutrient elements in a plant organism. Manganese takes part in a number of important physiological and biological processes such as nitrogen metabolism, photosynthesis, breathing, the oxidation-reduction conditions in the cell [1–4].

The optimal content of manganese, its critical level and toxic concentration at which the growth is depressed and the yield decreased has been established for a great number of crops [5].

New accurate and reliable methods for the analysis of various objects containing traces of manganese should be searched for.

Spectral and chemical methods are constantly used for the determination of manganese. Most of the photometric methods are based on its oxidation to permanganate. The reagents suggested for the spectrophotometric determination of manganese include 3,4,5,6-tetrafluoro-2-carboxyphenylfluorone [6], 1-(2-pyridylazo)-2-naphthol [7], triphenylphosphonium [8], isophthaldihydroxamic acid [9], 1,10-phenanthroline [10], 8-hydroxyquinoline [11], 4-(2-pyridylazo) resorcinol [12], 1-(2-pyridylazo)-2-naphthol [13,14], N-diphenylbenzamidine [15]. Some of the above mentioned extraction methods are characterized by a long procedure, low selectivity [10–14], a low stability of the complexes obtained [8,9], low sensitivity [9].

No data on manganese determination with Crystal Violet can be found in the literature. The thiazine dyestuff Crystal Violet (CV) we suggest is a new reagent for determination of microquantities of manganese. Mn(VII) forms a stable ion-pair with CV. This can be used in developing an extraction-photometric method for manganese determination. The present paper presents the conditions needed for manganese determination with Crystal Violet (CV). This is an extremely simple and direct extraction for the determination of manganese (VII) microquantities. Manganese was determined in plants.

EXPERIMENTAL

Apparatus

Absorbance measurements were made on a UV-VIS spectrophotometer, Germany, with a 1 cm quartz cuvette, 250 nm.

Reagents

All reagents were of analytical–reagent grade. All solutions were prepared with distilled demineralized water.

Stock manganese (VII) solution. A 1×10^{-2} M aqueous solution was prepared by dissolving 0.395 g of KMnO_4 in 250 ml of distilled water. After 10 days the exact concentration of manganese (VII) was checked titrimetrically using oxalate titration. Working solutions containing 1×10^{-4} M Mn(VII) were prepared by dilution.

Crystal Violet $\text{C}_{25}\text{H}_{30}\text{N}_3\text{Cl}$ (CV, Reachim). 1×10^{-2} M aqueous solution was prepared by dissolving 0.4077 g of CV in 100 ml of distilled water. Other CV concentrations were prepared by appropriate dilution. The solutions were stable for months.

* Corresponding author. E-mail: deny_kostova@yahoo.com

Foreign ion solutions. Solutions of diverse ions for interference studies were prepared by dissolving the amount of each compound needed to give 10 mg/ml concentration of the ion of interest.

Buffer compositions were as follows: buffers of pH 1, 2, 3 were of aminoacetic acid plus HCl; buffers of pH 4, 5 were of acetic acid glacial plus NaOH; buffers of pH 6, 7 were of KH_2PO_4 plus Na_2HPO_4 .

1,2-Dichloroethane, p. a.; sulphuric, hydrochloric, phosphoric, nitric and perchloric acids at concentrations of 2, 1.2, 2, 1.55, 9 M, respectively, were used.

Procedure

Preparation of the calibration graph

Transfer an aliquot of the stock solution containing 2–22 μg of manganese (VII) to a 100 ml separatory funnel. Add 0.4 ml of Crystal Violet 1×10^{-3} M, 0.3 ml of hydrochloric acid 1.2 M. Dilute to ml with distilled water and shake with 3 ml of 1,2-dichloroethane for 30 s. Transfer the organic layer through a dry filter paper into a 1 cm cuvette and measure the absorbance at 250 nm against a similarly prepared reagent blank. Plot the amount of manganese in the sample solution against absorbance to obtain the calibration graph.

Determination of manganese in plant samples

A wet burning of the plant samples was carried out and a mixture of sulfuric and nitric acids was used for the oxidation of the organic substance. A portion of 2 g of air-dry plant material was placed into a Kjeldahl flask and moistened with 4 ml of distilled water, then 5 ml of conc. sulfuric acid and 10 ml of conc. nitric acid was added. The flask was slightly heated to avoid splashing of the solution, decomposition and fuming away of nitric acid. When all the organic material was oxidized, the solution was heated at a higher temperature for 10 min [16]. After cooling, the solution was diluted with water and filtered. Portions of 3 ml conc. H_2SO_4 , 2 ml conc. H_3PO_4 and 0.1 g potassium periodate were added for the oxidation of Mn(II) to Mn(VII). It was heated to the boiling point and the temperature was maintained for 10 min. After cooling, the solution was diluted with water. It was transferred into a 50 ml volumetric

flask and diluted to the mark with distilled water. The aliquot parts of this solution were taken for analysis.

In a 100 ml separatory funnel were introduced 0.3 ml hydrochloric acid 1.2 M, 0.4 ml Crystal Violet 1×10^{-3} M, and the aliquote of the prepared solution of a plant sample. It was diluted to a volume of the aqueous phase of 10 ml with distilled water and extracted with 3 ml of 1,2-dichloroethane for 30 s. The organic phase was filtered through a dry paper into a 1 cm cuvette, and the absorbance was measured at 250 nm. A blank was run in parallel in the absence of a plant sample. A calibration graph was constructed with similarly treated standards.

RESULTS AND DISCUSSION

Extraction of the complex into organic solvents and determination of maximum absorption wavelength

Manganese(VII) forms an ion-pair with the Crystal Violet triphenylmethane dye (CV). The solubility of the ion-associate in various solvents was investigated. Several organic solvents such as 1,2-dichloroethane, benzene, toluene, chloroform and chlorobenzene were tested as solvents for the extraction of the complex. It is not extractable into benzene, toluene, chlorobenzene, partially extractable into chloroform, and fully extractable into 1,2-dichloroethane. The absorption spectrum of the ion-pair in 1,2-dichloroethane is shown in Fig. 1. We chose 250 nm as the working wavelength because of the greater absorptivity at this wavelength.

Composition, stability and effect of time of the ion-association complex

The Bent-French [17] method showed that the extracted species was a 1 : 1 ion-associate of the dye cation CV^+ and the MnO_4^- anion.

The aqueous phase containing 1.98×10^{-5} M manganese(VII) was extracted as described in Procedure. The absorption was measured at 250 nm against time in 1-cm cells with 1,2-dichloroethane in the reference cell. It was established that the ion-pair had a high stability. The absorption did not change for over 15 days after extraction.

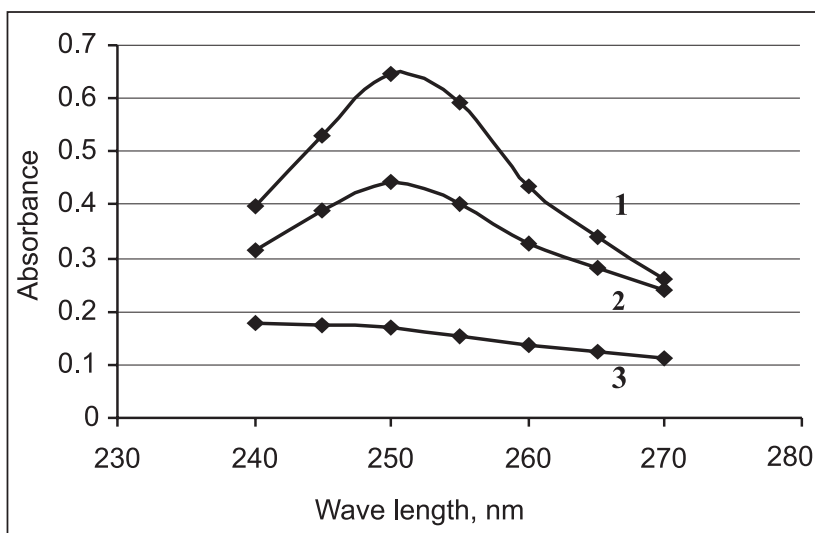


Fig. 1. Absorption spectra of the complexes: 1 – CV, 2 – Mn(VII) with CV, 3 – MnO_4^- extracted in 1,2-dichloroethane. $C_{\text{Mn(VII)}} = 1.98 \times 10^{-5}$ M, $C_{\text{CV}} = 2 \times 10^{-5}$ M, $C_{\text{HCl}} = 3.6 \times 10^{-2}$ M

The effect of reaction time was studied in the range 15 s – 2 min. Equilibrium between the two phases, aqueous and organic, was reached in 30 s (Fig. 2).

Photometric characteristics

A plot of the concentration of aqueous phase manganese (VII) vs. absorbance of the organic layer showed a good linearity in the range 0.2–2.2 μg of manganese (VII) per 1 ml of aqueous phase. The molar absorptivity of the complex was $(1.54 \pm 0.05) \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ at 250 nm, and Sandell's sensitivity was $3.57 \times 10^{-3} \mu\text{g cm}^{-2}$.

The reproducibility of the method was checked by analysing two series of solutions (10 determinations for each series) with the Mn(VII) concentration of 1 or 2 $\mu\text{g ml}^{-1}$. The relative standard deviation was found to be 0.9 and 0.6%, respectively.

Factors influencing complex formation

The acidity of the aqueous phase is a major factor in the determination. The change of the absorbance of the ion-associate in the pH range 1–7 was studied with buffers (Fig. 3). The effect of the type of mineral acid and its concentration on the interaction of manganese(VII) and Crystal Violet was studied. The

effect of various acids (phosphoric, hydrochloric, sulphuric, perchloric and nitric) on the extraction equilibrium was studied (Figs. 4, 5). The experimental data (Figs. 4, 5) showed that the maximum absorption for the ion-associate was obtained with hydrochloric acid in the range 0.24×10^{-1} – $0.48 \times 10^{-1} \text{ M}$. Figures 4 and 5 indicate that not only the concentration, but also the nature of the acid has an effect on the extraction equilibrium.

Optimization of the concentration of Crystal Violet (CV) is essential in the determination of manganese: for $1.98 \times 10^{-5} \text{ M}$ Mn(VII) the absorbance of the extract is maximum with a CV concentration $\geq 2 \times 10^{-5} \text{ M}$. The absorbance of the complex was not affected by an excess of the reagent (Fig. 6).

Effects of foreign ions

The effects of diverse elements and elements likely to form complexes with Crystal Violet were examined. Various salts and metal ions were added individually into the solution containing 10.9 μg of manganese, and the general procedure was applied. The possible interferences with the extraction and determination of manganese(VII) were examined, assuming an error of 1.5% in the absorbance reading as tolerable (Table 1). Most of the study salts did not interfere at the milligram level.

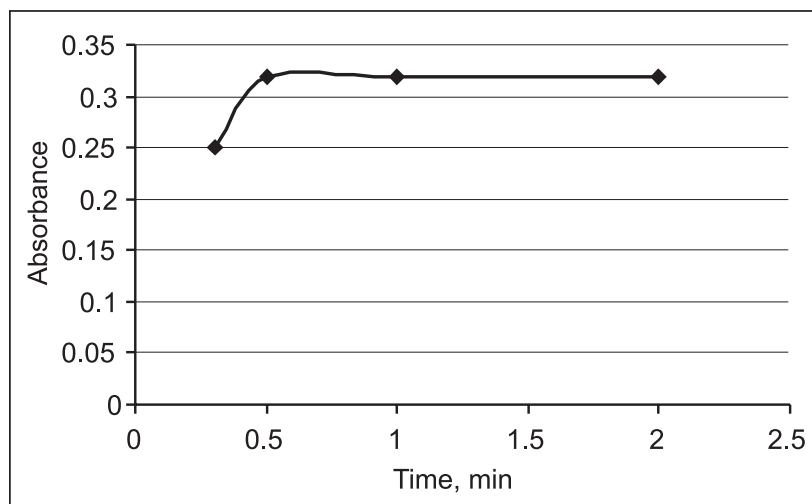


Fig. 2. Dependence of absorbance on extraction time. $C_{\text{Mn(VII)}} = 1.98 \times 10^{-5} \text{ M}$, $C_{\text{HCl}} = 3.6 \times 10^{-2} \text{ M}$, $C_{\text{CV}} = 3 \times 10^{-5} \text{ M}$

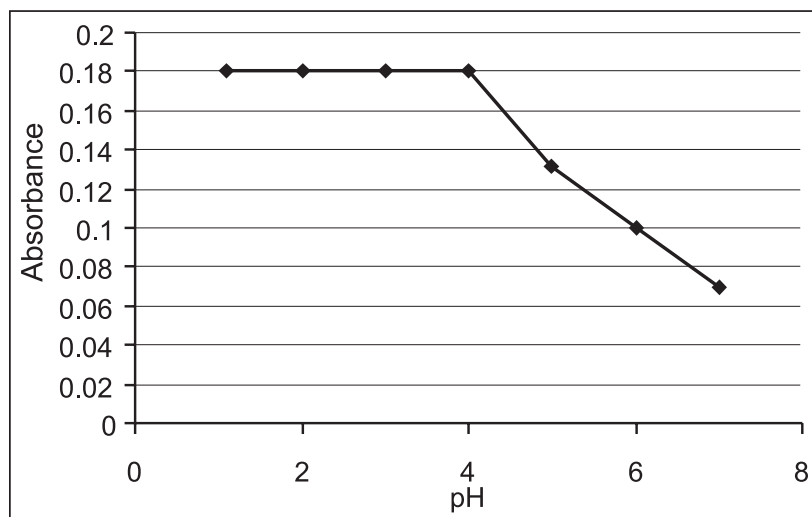


Fig. 3. Effect of pH and buffer constituents on Mn(VII) absorbance with Crystal Violet: $C_{\text{Mn(VII)}} = 1.98 \times 10^{-5} \text{ M}$, $C_{\text{CV}} = 4 \times 10^{-5} \text{ M}$

Fig. 4. Influence of acidity (1 – HClO_4 , 2 – H_3PO_4) on Mn(VII) extraction with Crystal Violet: $C_{\text{Mn(VII)}} = 1.98 \times 10^{-5} \text{ M}$, $C_{\text{CV}} = 4 \times 10^{-5} \text{ M}$

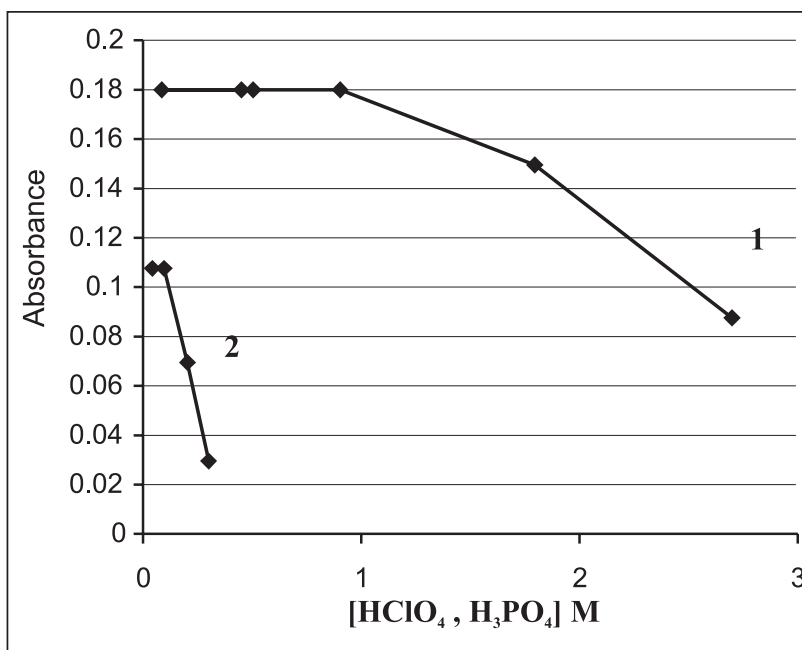


Fig. 5. Influence of acidity (1 – HCl , 2 – HNO_3 , 3 – H_2SO_4) on Mn(VII) extraction with Crystal Violet: $C_{\text{Mn(VII)}} = 1.98 \times 10^{-5} \text{ M}$, $C_{\text{CV}} = 4 \times 10^{-5} \text{ M}$

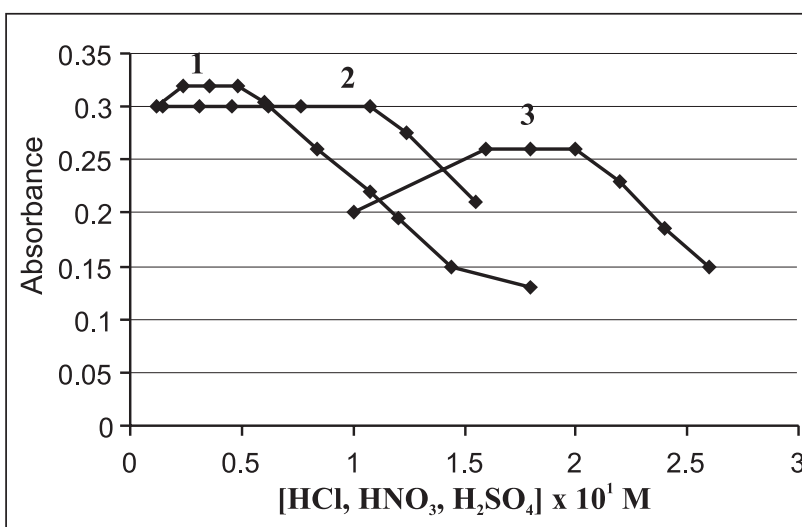


Fig. 6. Dependence of the absorbance on the concentration of Crystal Violet; $C_{\text{Mn(VII)}} = 1.98 \times 10^{-5} \text{ M}$, $C_{\text{HCl}} = 3.6 \times 10^{-2} \text{ M}$

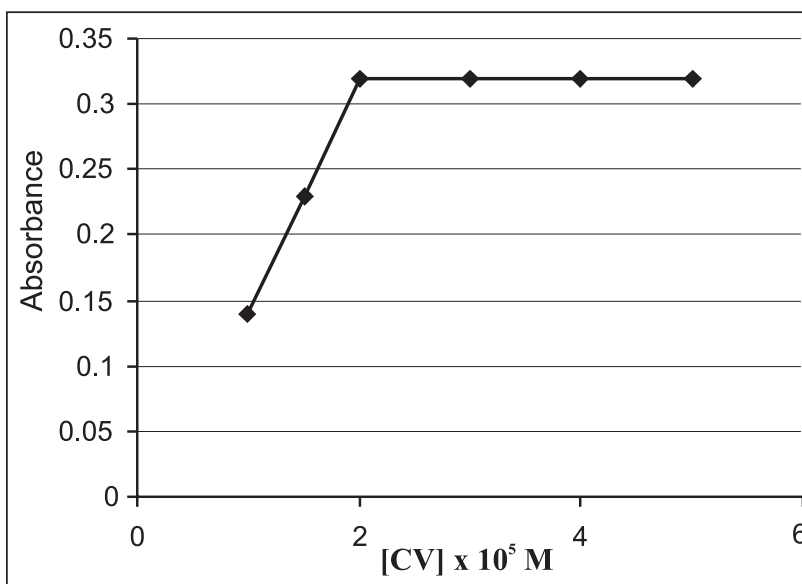


Table 1. Effect of foreign ions on the determination of 1.1 µg ml⁻¹ of manganese

Foreign ion or species	Limiting conc., mg
Mg(II)	475
BO ₃ ³⁻	250
Cd(II), Cu(II)	150
Pb(II)	100
Na(I), C ₂ O ₄ ²⁻	95
Mo(VI)	50
Br ⁻	40
K(I), PO ₄ ³⁻	30
Sr(II), ClO ₄ ⁻	20
Ni(II)	15
V(V)	12.5
Fe(III), Zn(II)	10
W(VI)	5
Ca(II)	0.2
Cr(VI)*, S ₂ O ₃ ²⁻	0.1
Hg(II)	0.04

* In the presence of masking reagents (tartrate).

The results show a possibility of the extractive-photometric determination of manganese(VII) in the presence of numerous ions without separation beyond the extraction procedure described above. Tartrate was used to eliminate the interference of Cr(VI). Thus, most of the common ions normally associated with manganese do not interfere in the determination of manganese by the proposed method. The proposed procedure can therefore be applied to the determination of manganese in plant samples without any prior separations.

Extraction equilibria

The following equilibria should be taken into account for the system of manganese(VII), Crystal Violet, hydrochloric acid, water and 1,2-dichloroethane.

1. Formation of the ion-association complex in the aqueous phase, and the corresponding equilibrium constant:

$$\beta = \frac{[\text{CV}^+\text{MnO}_4^-]}{[\text{CV}^+][\text{MnO}_4^-]}$$

2. Distribution of the complex between the aqueous and organic phases, and the corresponding distribution constant:

$$K_D = \frac{[\text{CV}^+\text{MnO}_4^-]_{\text{org}}}{[\text{CV}^+\text{MnO}_4^-]}$$

3. The entire extraction process and the corresponding extraction constant:

$$K_{\text{ex}} = \frac{[\text{CV}^+\text{MnO}_4^-]_{\text{org}}}{[\text{CV}^+][\text{MnO}_4^-]} = K_D \cdot \beta$$

The following solutions are introduced into 100 ml separating funnels: 1 ml of 1×10^{-3} M CV, 0.3 ml of 1.2 M hydrochloric acid, and the corresponding amounts of manganese(VII). The volume of the aqueous phase is brought to 10 ml with distilled water then it is extracted with 3 ml of 1,2-dichloroethane for 30 s. After the separation of the two phases, the organic phase is transferred through filter paper into a 25 ml flask and diluted to the mark with 1,2-dichloroethane. The light absorption of the organic phase is measured at 250 nm with a 1-cm light path cuvette. The absorbance (A) was measured against a reagent blank prepared in the same way (without manganese present).

To determine the distribution coefficient of TV, the absorptions obtained are compared to the one obtained after three extractions of the aqueous layer:

$$D_{\text{TV}} = A / A_{\text{max}} - A,$$

where A is light absorption for a single extraction, and A_{max} is light absorption for three extractions.

Using the logarithmic values of D_{TV} and the concentration of manganese, the plot log D_{CV} vs log C_{Mn(VII)} allows determination of the extraction values. The distribution constant is determined graphically by extrapolation of the straight line parallel to the x-axis up to the point of intersection with the y-axis. The slope of 45° confirms that a 1 : 1 ion-associate is formed.

The association constant of the study compounds is calculated on the basis of the dependence $K_{\text{ex}} = K_D \beta$ [18].

The values of the equilibrium constants characterizing the extraction equilibrium and the stability of the ion-association complex of Mn(VII) with CV were

$$K_D = 22.04 \pm 0.13,$$

Table 2. Comparison of the median values of manganese concentrations in the family Brassicaceae

Brassicaceae species	Mn, mg/kg CV method	Reliab. P = 99 %	RSD* % (n = 6)	Mn, mg/kg AAS method
Cauliflowers (<i>Br. oleracea</i> var. <i>botrylis</i> L.)	45.50	b	1.0	46.00
Savoy (<i>Br. oleracea</i> var. <i>sabauda</i> L.)	6.50	g	1.2	6.10
Brussels sprouts (<i>Br. oleracea</i> var. <i>gemmifera</i> D. C.)	5.00	g	0.7	5.50
Whete cabbage (<i>Brassica oleracea</i> L. var. <i>capitata</i>)	23.00	e	1.2	23.25
French turnip (<i>Br. oleracea</i> var. <i>gongilodes</i> L.)	15.40	f	1.5	15.80
Radishes (<i>Raphanus sativus</i> var. <i>minor</i> D. C.)	30.00	c	0.9	29.60
Kohlrabi	25.70	d	1.4	25.30
Broccoli	76.50	a	0.8	77.00

a, b, c – reliability degree.

* Relative standard deviation for CV method (based on six replications).

$$K_{\text{ex}} = (1 \pm 0.1) \times 10^4,$$

$$\beta = (4.54 \pm 0.05) \times 10^2.$$

Applications

In order to extend its utility, the proposed method was used for the extraction and spectrophotometric determination of manganese(VII) content in plant samples.

Manganese content in more widely used sorts of the family Brassicaceae was studied in order to establish the kind of differences in respect to the level of manganese in their production (Table 2). Manganese is actively absorbed by plants. The formation of plant mass depends on manganese supply.

The accuracy of the method was checked up by the atomic-absorption method. The experimental data (Table 2) showed a good agreement between the results obtained by the two methods. The experimental data by both methods have shown that the proposed extraction-photometric method with Crystal Violet can be successfully used for the determination of manganese microquantities in plant material. This is an extremely simple and direct method for the determination of manganese microquantities.

A comparative analysis of the reliability of differences among the mean values of manganese concentrations obtained for the family Brassicaceae in Table 2. The content of manganese in each species of this family is different, as the differences among the mean values are statistically proved [19, 20].

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D. Kostova, M. Kamburova

SKYSTINĖ MANGANO (VII) EKSTRAKCIJA NAUJU ANALITINIŲ REAGENTŲ

Santrauka

Pateiktos optimalios sąlygos spektrofotometriniam mangano (VII) nustatymui skystinės ekstrakcijos būdu, naudojant trifenilmetano dažą Kristalinį Violetinį (KV). KV pasiūlytas kaip naujas reagentas mangano (VII) mikroikiams nustatyti spektrofotometriu būdu. MnO_4^- : KV^+ molinis santykis sudaro 1 : 1. Rūgščiuose tirpaluose manganas (VII) sudaro su KV mėlyną kompleksą, kuris gali būti ekstrahuotas 1,2-dichloretanu. Komplekso optinės absorbcijos maksimumas yra ties 250 nm. Bero dėsnis yra išlaikomas $0,2\text{--}2,2 \mu\text{g} \cdot \text{ml}^{-1}$ mangano (VII) koncentracijos ribose. Komplekso molinis ekstinkcijos koeficientas sudaro $1,54 \cdot 10^4 \text{ l} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$, o Sandell jautrumas siekia $3,57 \cdot 10^{-3} \mu\text{g} \cdot \text{cm}^{-2}$. Ištirta įvairių katijonų ir anijonų įtaka mangano nustatymui. Pasiūlytasis naujas metodas yra labai jautrus, spartus ir pasižymi geru atsikartojamumu. Metodas buvo pritaikytas pėdsakiniam mangano kiekiams augaluose nustatyti.