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ANALYSIS OF LAVENDER AND ROSE OIL. STUDIES ON THE POSSIBILITY FOR ELABORATION OF A METHOD FOR KINETIC SPECTROPHOTOMETRIC DETERMINATION OF MANGANESE (II) IN BULGARIAN LAVENDER AND ROSE OIL

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ABSTRACT

The possibility for elaboration of a method for kinetic spectrophotometric determination of manganese (II) in Bulgarian lavender and rose oil was studied. The catalytic effect of manganese (II) on the oxidation of diphenylamine-4'-azobenzene-4-sulfonic acid, a potassium salt, with potassium periodate in the presence of 1,10-phenanthroline in weakly acidic media was used for this purpose. Lavender and rose oil samples (0,2-0,5 g) were dissolved by acid digestion procedure – 8-10 ml concentrated nitric acid and 1-2 ml concentrated perchloric acid. Manganese (II) in the range 0,05 – 2,5 ng ml^{-1} in the solution can be determined by the fixed-time method with a detection limit of 0,017 ng ml^{-1}.

Keywords: manganese (II) determination, catalytic kinetic method, spectrophotometry, diphenylamine-4'-azobenzene-4-sulfonic acid potassium salt, Bulgarian lavender oil, Bulgarian rose oil.

INTRODUCTION

The great number of publications on the subject of the quantitative determination of manganese in various objects explains the interest in this element. Manganese is an essential trace element for the human organism, but it can also be toxic. Therefore, various methods for its determination in soils, water, air, foodstuffs, drinks, medicinal plants and the drugs prepared from them, biological liquids, tissues and organs have been developed.

The need for the present research has emerged due to the lack both of a Bulgarian State Standard and of European standards for the determination of manganese in essential oils. Since the requirements to the qualities of the latter are getting ever higher, there is a need to develop and introduce methods for the determination of the content of various elements, among them manganese, in rose and lavender oil. The published methods for determination of manganese in various objects are chiefly related to instrumental atomic absorption ones - flame and electrothermal atomic absorption spectrometry (FAAS, ETAAS), Inductively Coupled Plasma Atomic Emission Spectroscopy (ICP-AES), etc.

The goal of the present studies is to clarify the possibility for developing a method by which to perform kinetic spectrophotometric determination of manganese (II) in Bulgarian lavender and rose oil. A starting point in the research were the catalytic spectrophotometric methods for determination of manganese in various objects published by K. Mutafchiev [1-4, 17]. There is none such among them that could be directly applicable to lavender and rose oil.

The most frequently used oxidizers in the kinetic methods for determination of manganese (II) based on its catalytic effect on the oxidation of organic substances are potassium periodate and hydrogen peroxide. Some

of the organic substances used are: hydroxyanthrochinons [5], triphenylmethane dyes [6], azo dyes [7, 8] and Schiff bases [9-16].

In the present research, the potassium salt of diphenylamine-4'-azobenzene-4-sulfonic acid (DAABSA) was used. In the kinetic system the catalytic action of manganese (II) on the oxidation of DAABSA with potassium periodate in the presence of 1,10-phenanthroline (phen) was used. As a result of the research, a catalytic kinetic spectrophotometric method for determination of manganese (II) by the fixed-time method in lavender and rose oil is proposed.

In order to obtain preliminary information on the distribution of manganese between the lavender plant and lavender oil, as well as rose blossom – rose oil, the manganese content of lavender plants and of rose blossom, from which the lavender and rose oils were obtained respectively, was determined.

EXPERIMENTAL

Reagents, instruments and equipment

The acids used were:

• nitric acid – Merck GR for analysis ISO 1.00456.2500;

• perchloric acid – Merck GR for analysis ACS, ISO 1.00519.2514.

All the other reagents were analytical grade. For the preparation of water solutions, twice distilled water was used. Before any measurements, the solutions were kept in polypropylene vessels.

The standard manganese (II) solution with concentration 0,0182 mol l^{-1} was prepared from manganese sulfate (analytical grade) and was diluted immediately before making the measurement. The concentrations of the other solutions were the following: DAABSA 0,00085 mol l^{-1}; potassium periodate 0,01 mol l^{-1}; phen 0,01 mol l^{-1}; trisodium citrate 0,056 mol l^{-1}. The buffer solution with pH=3 was prepared by mixing 0,1 mol l^{-1} acetic acid with 0,1 mol l^{-1} potassium dihydrogen ortophosphate in proportion 2,33:1.

The absorption of the solutions was measured in a 10 mm tube and a Specol 11 spectrophotometer. A NBE ultrathermostat was used for temperature control. The atomic absorption analysis was performed by means of a Perkin-Elmer Zeeman 5000 atomic absorption spectrophotometer

Procedure for preparation of the samples for analysis

On analytical scales, in a 25 ml beaker, 0,2 – 0,5 g of lavender or rose oil were measured. The sample was filled with 8-10 ml concentrated nitric acid, the beaker was covered with a watch glass and left for 12 hours. It was heated on a sand bath until the emission of nitrogen oxides ceased. After cooling of the sample, 1-2 ml concentrated perchloric acid was added and the solution was heated until its volume was reduced by half. 10 ml twice distilled water was added and it was filtered through a Blue Ribbon filter paper. The filtrate was collected in a 25 ml flask. 1-2 ml of concentrated nitric acid was added and distilled water was added up to the 25 ml mark.

The weighed samples of lavender or rose blossom were subjected to wet mineralization in an analogous way.

In parallel, a blank sample was prepared from all used reagents.

Procedure for kinetic-spectrophotometric determination of manganese in the solutions

0,25 ml of the reagent DAABSA and 0,5 ml of the test solution, prepared in advance in such a way so that its manganese (II) content would be in the range 0,25 – 12,5 ng of manganese (II), were poured into a 10 ml test-tube. 4,25 ml mixture of phen, trisodium citrate, potassium periodate solutions and buffer solution (prepared immediately before measuring) was added in proportion 1+1+4+79. The tube was placed inside the thermostat for a period of 6 min at temperature 80°C. It was cooled down quickly in a vessel full of water and ice for termination of the reaction. The solution was transferred to the tube and the absorption was measured at 445 nm compared to the blank. Based on the measured absorption, the manganese (II) content was determined.

In the determination of manganese in lavender and in rose blossom, it was necessary to dilute considerably the initial solutions due to the high manganese content.

RESULTS AND DISCUSSION

When DAABSA is oxidized with potassium periodate in weakly acidic media, reduction of the colour intensity of the solution is observed. Fig. 1 shows the

absorption spectra of DAABSA, DAABSA + potassium periodate, DAABSA + potassium periodate + phen, DAABSA + potassium periodate + Mn (II) and DAABSA + potassium periodate + phen + Mn(II) after heating at 80°C for a period of 6 min according to the procedure. Based on the figure, the conclusion can be made that the oxidation of DAABSA with potassium periodate is a slow reaction, which, however, is catalyzed by the presence of small quantities of manganese (II). The reaction can also be accelerated in the presence of phen and especially in the presence of phen and manganese (II). The absorption maximum is at 445 nm, and it was at this value that the following measurements were made. The optimized conditions for determination of manganese were the following: concentration of the reagent DAABSA 0,0000425 mol l^{-1}; potassium periodate 0,0004 mol l^{-1}; phen 0,0001 mol l^{-1}; pH=3; temperature of the thermostat 80°C; reaction time 6 min. Fig. 2-5 show the dependence of the absorbance from the temperature, pH of the environment, the concentration of potassium periodate and the concentration of 1,10-phenanthroline.

When the interfering influence of various ions that may be found in acidic water solutions was studied, it was established that there is such an influence when the relation of the concentration of the interfering ion (ng/ml) to the concentration of manganese (II) (ng ml^{-1}) is greater than: for cobalt (II) 50:1; iron (III) 70:1, but in the presence of trisodium citrate, 1200:1; chrome (III) 170:1; copper (II) 250:1; zinc (II) 350:1, but in the presence of trisodium citrate, 1300:1; nickel (II), cadmium (II), mercury (II) 1000:1, lead (II) 3000:1; aluminum (III) 4000:1; fluoride ions 30000:1; calcium (II), magnesium (II), barium (II), chloride ions, sulfate ions, borate ions, phosphate ions and acetate ions 100000:1.

Based on the optimized conditions, a calibration curve was constricted, the rectilinear part of which is in the range 0,05 – 2,5 ng ml^{-1} manganese (II). The regression equation of the calibration curve is A=0,010 + 0,246 C, where C is the concentration (ng ml^{-1}), A is the difference between the absorbance of solutions containing DAABSA in the absence of Mn (II) and this in the presence of Mn (II) after the end of the kinetic reaction, and the correlation coefficient is 0.997.. The proposed method has relative standard deviation 8,1% per 10 determinations of manganese (II). The detection limit is 0,017 ng ml^{-1} Mn(II).

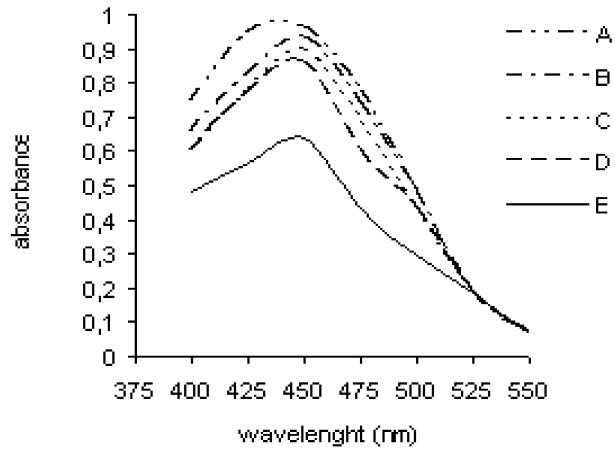

Fig. 1. Absorption spectra of DAABSA, (A); DAABSA + potassium periodate, (B); DAABSA + potassium periodate + phen, (C); DAABSA + potassium periodate + Mn (II), (D); and DAABSA + potassium periodate + phen + Mn(II), (E); DAABSA, 4.25x10^{-5} mol l^{-1}; KIO_4, 4x10^{-4} mol l^{-1}; Mn (II), 1ng ml^{-1}; phen, 1x10^{-4} mol l^{-1}; pH 3; 80°C; 6 min.

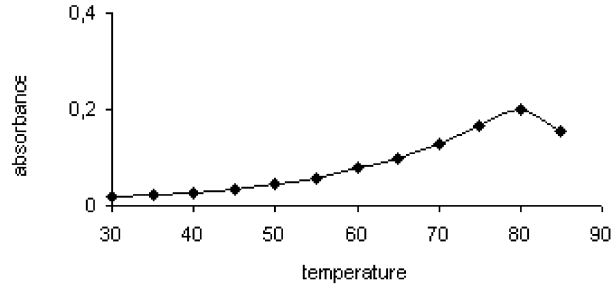

Fig. 2. Dependence of the absorbance from the temperature (°C).

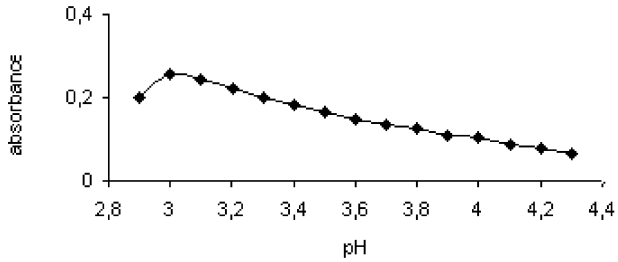

Fig. 3. Dependence of the absorbance from pH of the environment.

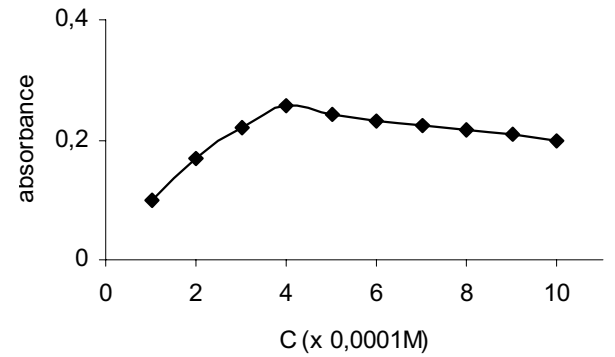

Fig. 4. Dependence of the absorbance from the concentration of potassium periodate.

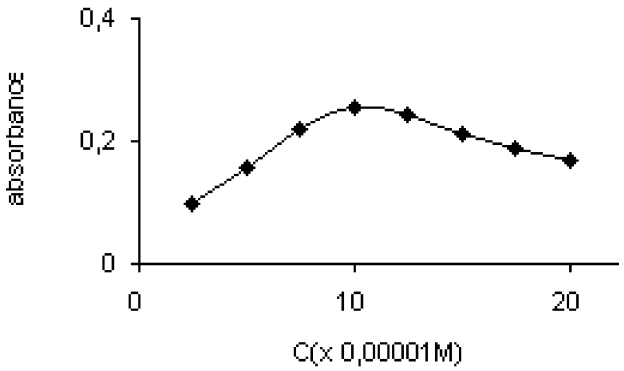

Fig. 5. Dependence of the absorbance from the concentration of 1,10-phenanthroline.

Table 1. Manganese (II) Content of Real Samples from the Territory of the Republic of Bulgaria (μg g^{-1}).

	Proposed method	FAAS
Lavender oil	0.8±0.08	0.9±0.1
Lavender	39±5	42±6
Rose oil	7±0.8	6±0.8
Rose blossom	23±2	24±3

Table 1 shows the results of the quantitative determination of manganese in samples of lavender oil, lavender, rose oil and rose blossom. The results are compared to results from Flame Atomic Absorption Spectrometry (FAAS).

CONCLUSIONS

A method for kinetic-spectrophotometric determination of manganese (II) in Bulgarian lavender and rose oil has been developed.

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