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Autor: Jiménez, Ana María / Herrador, M.A. / Asuero, A.G.

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Kurze Mitteilung — Communication brève

Spectrophotometric Determination of Copper in Vinegar with Glyoxal bis (4-phenyl-3-thiosemicarbazone)

Ana María Jiménez, M. A. Herrador and A. G. Asuero
Faculty of Pharmacy, Seville

Introduction

Copper can be present in many wines either as a consequence of their use in vineyard sprays (1) or its dissolution from containers, as well as owing to its natural presence in grape. Copper has been considered as one of the most undesirable contaminants. When it is present at concentration as low as a few $\mu\text{g ml}^{-1}$ it has a noticeable effect on the taste of beverages, e. g. whisky and wine, and also tends to form deposits over long storage periods (2–3). In addition, a copper content in excess of $10 \mu\text{g ml}^{-1}$ usually contributes to the development of off flavours during short periods of shelf life. Such conditions downgrade beverages in quality, e. g. wine; as a result consumer acceptance decreases. The industry has assumed this problem and requires simple, sensitive and rapid test methods for copper.

An accurate, yet relative simple technique for determining trace amounts of copper in wine vinegar is required for use by unskilled personnel in the control plant. The ideal procedure would be one in which preliminary ashing is eliminated and sufficiently large sample can be taken to ensure an adequate measurable concentration of copper. It has been shown (4) that copper proteins lose their copper content in acid solution below pH 3.0. Both cupric and cuprous copper are lost, the latter being oxidised in the acid aqueous solution. Due to the acidic nature of vinegar which has $\text{pH} < 3$ the proteins are hydrolysed to amino acids (5), and it is therefore sufficient to transfer the copper in vinegar to the form of free cupric ions by reducing the pH to about 1.

Spectrophotometric methods for determining copper in foods involve usually the use of reagents of the dithiocarbamate and cuproine types (6–7). Many of the cuproine type reagents are the product of difficult and tedious synthesis and, hence, are high in cost. On the other hand, the dithiocarbamate type reagents for copper, although easily available, require liquid-liquid extraction which is undesirable in a laboratory where many simultaneous determinations are often required. In the present paper the spectrophotometric method for copper (8) which use glyoxal bis (4-phenyl-3-thiosemicarbazone) (9) (GBPT) as chromogen reagent

has been applied to the determination of copper content in vinegar. For the purpose of this investigation, spectrophotometric determination of copper as a bathocuproine disulphonate complex (10–11) was chosen as the standard for which reliable comparative data could be obtained.

Experimental

Apparatus

A spectrophotometer (Bausch & Lomb Spectronic 2000) and 1-cm-matched cells were used for the spectrophotometric measurements. The pH of the final solution was measured using a Beckman Model 70 pH meter and an Ingold combination glass electrode.

Reagents

Glyoxal bis (4-phenyl-3-thiosemicarbazone) was used as a 0.1% W/V solution in dimethylformamide (9).

Bathocuproine disulphonate (Sigma No B-1125).

All the other reagents were of analytical reagent grade.

Procedure for the determination of copper in vinegar with GBPT

Into a 10-cm calibrated flask transfer a volumen of vinegar (up to 3.2 ml), add 0.4 ml of sulphuric acid (1 + 3 V/V) and 5.2 ml of dimethylformamide. Mix thoroughly, add 0.8 ml of 0.1% W/V GBPT solution in dimethylformamide, dilute to exact volume, mix again and measure the absorbance at 487 nm against a reagent blank prepared under the same conditions.

Pipette another sample aliquot of vinegar so that the background absorbance can be determined. Treat this second aliquot exactly the same as the test solution without the addition of GBPT. Measure the background absorbance against a solvent blank and subtract it from the absorbance of the test solution.

Use the absorbance reading to find the concentration of copper (II) in the original aliquot of vinegar. Take 0.12, 0.20, 0.40, 0.60, 1.20 and 1.60-ml-portions of a $25 \mu\text{g ml}^{-1}$ standard copper solution — freshly prepared — through this procedure to construct a calibration curve. The molar absorptivity coefficient is $11.800 \text{ l mol}^{-1} \text{ cm}^{-1}$.

Determination of copper in vinegar with bathocuproine disulphonate (BCDS)

The general procedure followed was similar to that reported by Friess (12) for bathocuproine, and adapted to an homogeneous medium.

Results and discussion

The samples for analysis were all various types of unaged vinegars produced in several plants from Andalusia country (Spain). The various vinegar samples are listed in table 1 and where purchased from the local market.

Table 1. Vinegar sample identification and type

| Samples No | pH | Weight of 5 ml samples g | Winery origin / Trade name | Volume taken ml | Fe found $\mu\text{g ml}^{-1}$ |
|------------|------|--------------------------|---|-----------------|--------------------------------|
| I | 2.76 | 5.043 | Chiclana/Collantes Primitivo S. A. | 0.3 | 6.77 ± 0.45 |
| II | 2.83 | 5.049 | Jerez de la Frontera/M. Gil Galán S. A. | 0.3 | 6.54 ± 0.52 |
| III | 2.52 | 5.007 | Palma del Condado/Raw vinegar | 0.2 | 19.38 ± 0.16 |
| IV | 3.00 | 5.002 | Bollullos Par del Condado/Raw vinegar | 0.2 | 20.31 |
| V | 2.85 | 5.090 | Jerez de la Frontera/Bobadilla | 0.2 | 19.97 ± 0.64 |

No sample preparation was necessary. Samples were stored at low temperature in the refrigerator and were filtered before determination in order to remove any suspended material. The alcohol concentrations normally encountered in vinegar are low and do not affect the colour intensity of the Cu-GBPT complex. In the acidic solution employed, none of the metallic constituents which may be present in vinegar interfere with the copper-GBPT colour development (9). Table 2 shows results obtained by using the GBPT and BCDS procedures to measure copper in samples of vinegar taken from representative bottles of different brands. The iron content of vinegar was determined by the o-phenanthroline method (12) for the sake of comparison. It was found that a correction had to be made for coloured material from vinegar which absorbs to some extent at 487 nm (GBPT), 410 nm (BCDS) and 508 nm (o-phenanthroline). This was achieved by making triplicate analysis which were identical to those described under procedures except that the GBPT (or the o-phenanthroline when analysing iron) was purposely omitted.

Table 2. Determination of copper in vinegar samples by the GBPT and BCDS methods

| Sample No | GBPT Method | | | BCDS Method | | |
|-----------|-----------------|------------------------------------|------------------------------------|-----------------|------------------------------------|------------------------------------|
| | Volume taken ml | Blank absorbance $\bar{x} \pm s_d$ | Copper found $\mu\text{g ml}^{-1}$ | Volume taken ml | Blank absorbance $\bar{x} \pm s_d$ | Copper found $\mu\text{g ml}^{-1}$ |
| I | 3 | 0.093 ± 0.004 | 1.03 ± 0.02 | 3 | 0.128 | 0.995 ± 0.009 |
| II | 3 | 0.123 ± 0.005 | 0.70 ± 0.07 | 3 | 0.166 ± 0.006 | 0.50 ± 0.02 |
| III | 3 | 0.386 ± 0.001 | 3.26 ± 0.04 | 3 | 0.541 ± 0.007 | 3.23 ± 0.12 |
| IV | 2 | 0.048 ± 0.008 | 3.58 ± 0.02 | 2 | 0.079 ± 0.007 | 3.38 ± 0.06 |
| V | 2 | 0.154 ± 0.003 | 15.92 ± 0.09 | 0.5 | 0.005 ± 0.002 | 15.73 ± 0.17 |

A comparison of the results obtained shows acceptable agreement between the two procedures for samples I, III and V. Samples II and IV give a lower copper content with the BCDS method. Many complex organic compounds are expected to be present in vinegar and it seems reasonable to assume that some of these compounds, particularly those which are carboxylic or polyhydric in nature, will tend to complex with any copper ion present, given the relatively high pH value (pH 4–7) at which the determination according to the BCDS method is carried out. However, the results found after dry ashing of the vinegar samples II and IV and further determination of copper by AAS (5) or by the BCDS method, were comparable to the results obtained by the direct determination with GBPT.

The vinegar samples analysed, with the exception of sample V, fulfil the requirements of the Spanish Hygienic Regulations (13) which set a legal limit for copper in vinegar of $10 \mu\text{g ml}^{-1}$. Values obtained in this paper were of the order found by Villanua et al. (14), but lower than those found by Peña et al. (15) in wine vinegar samples.

Summary

Both glyoxal bis (4-phenyl-3-thiosemicarbazone) and bathocuproine disulphonate methods for copper have been applied in this paper to the determination of the copper content of a variety of vinegars produced in different plants from the Andalusia country. It has been shown that for routine determination the first procedure is fast and sufficiently precise and it fits well into a program where large number of analysis are to be made. The copper content of the six samples analysed ranged from 0.50 to $15.73 \mu\text{g ml}^{-1}$.

Zusammenfassung

Beide, die Glyoxal bis (4-phenyl-3-thiosemicarbazone)- und die Bathocuproindisulphonat-Methode für Kupfer, wurden in dieser Studie benutzt, um den Kupfergehalt von verschiedenen Essigsorten, die in Andalusien produziert wurden, zu bestimmen. Es wurde gezeigt, dass für die Routinebestimmung das erstere Verfahren schnell und hinreichend präzise ist, und es sich gut in ein Programm einfügt, in dem eine grosse Anzahl von Analysen zu machen ist. Der Kupfergehalt der sechs analysierten Sorten reicht von 0,50 bis $15,73 \mu\text{g ml}^{-1}$.

Résumé

Les méthodes spectrophotométriques avec comme réactifs le glyoxalbis (phényl-4 thio-3 semicarbazone) et la bathocuproïne disulfonique ont été appliquées au dosage du cuivre de divers vinaigres produits dans différentes régions d'Andalousie. On peut admettre que la première méthode est assez rapide et assez précise pour être appliquée aux dosages de routine. La teneur en cuivre des six échantillons analysés se situe entre 0,50 et $15,73 \mu\text{g ml}^{-1}$.

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Dr. A. G. Asuero
Department of Analytical Chemistry
Faculty of Pharmacy
The University of Seville
E-41012-Seville