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DETERMINATION OF NICKEL IN TEA BY USING DIMETHYLGLYOXIME METHOD

Review: **Professor Elżbieta Łodyga-Chruścińska, Ph.D., D.Sc.**

Tea is one of the most popular beverages in the world. Recent studies have shown that it contains concentrations of heavy metals such as nickel. Heavy metals are known to be toxic and there have been many studies on their toxicity such as lead and cadmium, however researchers are now starting to explore the nature of the toxicity of nickel. A common and well-known method of spectrophotometric determination of nickel by dimethylglyoxime reagent was used. The presented paper, due to the increasing concerns surrounding the harmful effects of nickel compounds, aims at testing and demonstration of the effectiveness of the mentioned method.

Introduction

Tea is one of the most popular beverages in the world. The health benefits of tea have been extensively documented. Some recent studies have shown that it contains concentrations of heavy metals such as nickel. Studies conducted by S. Seenivasan et al. determined the concentration of nickel in black teas from South India using atomic absorption spectrophotometer to be on average 2.53 ± 1.01 mg/kg. They found that the nickel concentration varied in different samples and attributed these variations to the application of low quality fertilizers [1].

Heavy metals are known to be toxic and there have been many studies on the toxicity of metals such as lead and cadmium, however researchers are now starting to explore the nature of the toxicity of nickel [2, 3]. DNA micro-array analysis performed by Koji Kawata et al. showed that heavy metals like Ni altered the expression of certain genes [4]. Max Costa's et al. studies review (1998) and the study (Costa et al. 2005) of the molecular biology of nickel carcinogenicity indicated that although soluble nickel salts were generally non-carcinogenic, certain nickel compounds that could yield Ni^{2+} ions were capable of de-activating tumor suppressor genes [5, 6]. Research carried out by Ionescu et al. showed that there is an increased level of transition metals like nickel in breast cancer tissue [7]. While a research group lead by Haber (2000) performing a hazard identification and dose-response for nickel salts found that apart from its possible carcinogenic effects ingestion of soluble nickel salts could also cause health risks such as systemic effects on the kidney, on neonatal mortality and on the immune system [8]. Their studies also showed that exposure to soluble nickel in drinking water was carcinogenic in various breeds of rats and mice. Recently, the USDA (United States Department of Agriculture) published that the upper intake level of nickel that would pose no health threat was 1mg/day. Nickel causes more hypersensitivity than any other metal and research conducted by the asthma and allergy centres indicated that 14.2% of the population suffers from nickel hypersensitivity [9, 10].

Due to the prevalent nature of nickel hypersensitivity it is important to study the efficiency of various methods in the determination of nickel. A major interference in the estimation of nickel is the presence of cobalt, iron or copper [11, 12]. Thus, various methods have been developed to help eliminate this problem. One of them is the common, well known, sensitive and simple method which shows the complexometric reaction between nickel and dimethyglyoxime [13]. Nevertheless, the newest determinations of heavy metals in food are based on atomic absorption spectroscopy [14, 15].

In this study, the common and well-known method of spectrophotometric determination of nickel by dimethylglyoxime reagent was used. The paper, due to the increasing concerns surrounding the harmful effects of soluble nickel salts, aims at testing and demonstration of effectiveness of the mentioned method.

Methodology and experimental

Digestion is the most demanding step in sample preparation, and its aim is to break the sample into more simple constituents with the aid of time, heat and reagents using different devices. Microwave heating emerged in the analytical field to dramatically improve the conventional wet digestion procedures with conductive heating that took several hours and reduced them to minutes in many cases. Additionally, the development of on-line microwave systems has proved them to be simple, relatively safe to use, provide a decrease in the blank values, reduce the

contamination risk when completely closed systems are used, applicable to samples of different natures and completely fit for automation. The most outstanding advantage of the microwave digestion systems is their tremendous potential in performing efficient and reproducible digestion and/or mineralization of different kinds of samples with minimum operator attention. Furthermore, the totally closed manifolds provide minimum exposure to the environment and in consequence minimum contamination and/or losses of volatile elements [16].

The method consists of a digestion with hot concentrated acid, in closed containers in diffuse microwave ovens or in open containers in microwave focus of aqueous samples unaltered dissolve metals associated with particles or present in colloidal form and/or organic. The digestion of aqueous samples such as this, which may occur in a more or less drastic conditions gives an estimate of the total metal, which is a function not only of the conditions experiments also the specific properties of the metal [16].

Ultraviolet-visible spectrophotometer-molecular absorption spectroscopy in the ultraviolet (UV) and visible (VIS) is concerned with the measured absorption of radiation in its passage through a gas, a liquid or a solid [17].

The intensity of light passing through the samples (I) is compared with the intensity of light before it passes through the sample (I_0) .The I/I_0 rate is called the transmittance, and is usually expressed as a percentage (T). The absorbance, A, is based on the transmittance: A = -log(T). The basic parts of a spectrophotometer are a light source, a holder for the sample, a diffraction grating or monochromator to separate the different wavelengths of light, and a detector. The detector is typically a photodiode or a CCD (Charge Coupled Device). Photodides are used with monochromators, which collect light of different wavelengths on different pixels. Samples are typically placed in a transparent cell, known as a cuvette. Cuvettes are commonly used with an internal width of 1cm. Our experiment provides the determination of nickel in different kind of teas [17].

Microwave digestion

The 17 different samples of tea including black, green and aromatic teas were collected. 5 g of each tea sample was weighed. Distilled water was boiled in an electric kettle and in a beaker. Then, the samples were transferred into 25 ml of boiling water and kept for 5 min.

The system used for the microwave digestion of the samples was a Maxidigest MX 350 microwave digester (Prolabo, Paris, France). The samples were completely decomposed by mixture of concentrated acids [65% HNO_3 and 70% $HClO_4$] as well as using of heating at 125 W within 15 minutes. Decomposed samples were filtered and then made up to 50 ml using distilled water in a volumetric flask.

Spectrophotometric measurements

Spectrophotometer has been used on covering the wavelength 530 nm: UV-Vis Spectrophotometer Hewlett Packard 8453 in a range 190-1100 nm (845x UV-Visible Chemstation Software).

All the used chemicals were of analytical-reagent grade. Dimethylglyoxime and nickel(II) sulfate hexahydrate pure were purchased from POCH S.A. Throughout all analytical work double distilled water was used. Water was purified using a Pure Lab Ultra apparatus from Elga, U.K.

Nickel, standard solution was prepared by dissolving 0.4478 g $NiSO_4*6H_2O$ in distilled water with addition of 2 ml concentrated sulfuric acid. 1 ml of prepared solution consists 0.10 mg Ni. The solution was stable for a year. Nickel, working standard solution was prepared by dilution of 10 ml of basic standard solution in a volumetric flask (100 ml) and stirred [13].

Dimethylglyoxime solution was done by dissolving dimethylglyoxime in ammonia and after adding water the solution was filtered. The solution had to be kept in dark bottle and it was stable for two weeks.

Ammonium citrate solution was made from citric acid monohydrate which was dissolved in ammonia solution.

In order to prepare calibration curve the following volumes of nickel working standard solution 0.0, 1.0, 2.5, 5.0, 10.0, 25.0 and 50 ml (responding to 0.00, 0.01, 0.025, 0.05, 0.10, 0.25 and 0.50 mg Ni in standard solution) were placed in seven clean volumetric flasks. Afterwards, 50.0, 49.0, 47.5, 45.0, 40.0, 25.0, and 0.0 ml of distilled water was added, respectively. 10 ml citrate ammonia, 5 ml iodine solution and 20 ml dimethylglyoxime solution were added to each flask. The samples were mixed thoroughly. The prepared standards were ready to be used after 10 min but not later than after 30 min. Samples were transferred to the cuvette (absorption cell) and measured absorption at the wavelength $\lambda = 530$ nm. The linear calibration curve was drawn as the function of absorption in different concentration of nickel ions [mg/ml]. The equation of the calibration curve was $y = 97{,}69427x + 0{,}02645$ and the coefficient correlation of the calibration curve was $R^2 = 0{,}99694$.

Mineralizated tea samples were mixed with distilled water to the volume 50 ml. 10 ml of citrate ammonia solution, 5 ml of iodine solution and 20 ml of dimethylglyoxime solution were added to nickel ions solutions. The samples were mixed thoroughly. The prepared standards were ready to be used after 10 min but not later than after 30 min. Samples were transferred to the cuvette (absorption cell) and measured absorption at the wavelength $\lambda = 530$ nm. The concentrations of Ni ions were read from the calibration curve, which was prepared earlier. The Ni content in the determined samples was showed in Table 1.

Results and discussion

The data obtained from the experiments is summarised below in Tables 1. Concentration of a nickel in teas has been determinated by the UV-Vis spectrophotometer with dimethylglyoxime method. The measurements have been repeated three times. Measurements of each sample have differed little from each other. Table 1 shows the average content of nickel from all 3 series of measurements with standard deviation.

Table 1

Nickel concentration in the tea samples [mg/kg]

Lp.	**Name of tea**	**Nickel content x±SD**
1.	Firm 1(black)	1.28±1.2
2.	Firm 2 (black)	1.90±0.2
3.	Firm 3 (black)	1.62±0.5
4.	Firm 4 (black)	0.45±0.5
5.	Firm 5 (black)	0.92±0.8
6.	Firm 6 (green)	1.66±0.2
7.	Firm 7 (green)	0.94±0.1
8.	Firm 8 (green)	1.37±0.1
9.	Firm 9 (green)	1.23±0.2
10	Firm 10 (green)	1.06±0.9
11.	Firm 11 (aroma)	1.02±0.7
12.	Firm 12 (aroma)	0.07±0.02
13.	Firm 13 (aroma)	0.03±0.02
14.	Firm 14 (aroma)	2.72±1.1
15.	Firm 15 (aroma)	0.71±0.5
16.	Firm 16 (aroma)	1.40±0.2
17.	Firm 17 (aroma)	1.38±0.2

These results clearly indicate that different tea samples contained nickel in various amounts. The level of the amount of nickel in examined teas varied from 0.06-2.72 mg/kg. The highest level of the content of nickel was found in the aroma tea sample, 2.72 mg/kg.

Application of dimethyloglioxime method in determination of nickel in the studied tea samples using UV-Vis spectrophotometer gives reasonable and not exorbitant data comparing with those found by the other authors [14, 15].

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OZNACZANIE NIKLU W HERBACIE METODĄ DIMETYLOGLIOKSYMOWĄ

Streszczenie

Herbata jest jedną z najbardziej popularnych używek na świecie. Metale ciężkie, na przykład takie jak kadm i ołów znane są jako substancje toksyczne. Wiele badań potwierdza ich toksyczność. Ostatnie badania pokazują, że herbata zawiera również śladowe ilości niklu. Obecnie, naukowcy poszerzają wiedzę na temat jego szkodliwości. W omawianej pracy, w celu oznaczenia zawartości niklu w herbacie, zastosowano prostą i dobrze znaną spektrofotometryczną metodę z użyciem dimetyglioksymu.

Celem niniejszej pracy ze względu na zwiększone zainteresowanie szkodliwymi wpływami związków niklu na organizmy żywe, było sprawdzenie i przedstawienie efektywności wyżej wymienionej metody.