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ORIGINAL PAPER

Determination of Trace Nickel in Hydrogenated Cottonseed Oil by Pressurized Bomb Acid Digestion and Graphite Furnace Atomic Absorption Spectrometry Detection

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Abstracts A pressurized polytetrafluoroethylene (PTFE) bomb method for the digestion of trace nickel in hydrogenated cottonseed oil prior to its determination by graphite furnace atomic absorption spectrometry (GFAAS) has been developed. Currently, the methods outlined in United States Pharmacopeial 28 (USP28) and British Pharmacopeial (BP2003) methods are recommended as the official methods for analyzing nickel in hydrogenated cottonseed oil. However, when using these methods, the samples were easily tarnished during sample pretreatment when using a silica crucible. In contrast, when using a platinum crucible, hydrogenated cottonseed oil acting as a reducing material may react with the platinum and destroy the crucible. In order to avoid the tarnish with a silica crucible and the risk when using platinum, the technology of a pressurized PTFE bomb method was applied in the digestion of nickel in hydrogenated cottonseed oil. The results showed that hydrogenated cottonseed oil can be digested completely by the optimal combinations of HCl (0.1 mL) and HNO_3 (0.5 mL). The digested solution was investigated using graphite furnace atomic absorption spectrometry.

Keywords Hydrogenated cottonseed oil · GFAAS · Nickel

Introduction

Cottonseed oil is a vegetable oil extracted from the seeds of the cotton plant after the cotton fibers have been removed. Cottonseed oil has no cholesterol and is very low in *trans* fatty acids [1]. It is commonly used in manufacturing potato chips and other snack foods. Along with soybean oil, cottonseed oil is very often partially or fully hydrogenated [2]. Hydrogenated cottonseed oil is used in candle production and as a drug additive.

In hydrogenation of cottonseed oil, nickel is commonly used as a catalyzer in the chemosynthesis industry [3], so that the excess nickel may be found in the industrial production of hydrogenated cottonseed oil. Excess nickel can cause adverse health effects including allergic reactions, lung cancer, oral cavity cancer and larynx cancer [4].

Thus, the determination of nickel in hydrogenated cottonseed oil becomes very important. To our knowledge, few papers have reported the analytical methods of nickel determination in hydrogenated cottonseed oil [5]. Currently, the methods used for the analysis of nickel in hydrogenated cottonseed oil are those according to United States Pharmacopeial 28 (USP28) [6] or British Pharmacopeial (BP2003) [7]. However, in practice during the pretreatment, it was very difficult to avoid the high background noise when using a silica crucible. On the other hand, hydrogenated cottonseed oil acting as a reducing

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material may form a compound with platinum to destroy the crucible when a platinum crucible is used [8].

In this study, we proposed a practical pretreatment method which avoids tarnishing for the determination of trace nickel in hydrogenated cottonseed oil. In the pretreatment of hydrogenated cottonseed oil, the technology of a pressurized-PTFE-bomb acid digestion was applied to avoid the tarnishing and the risk involved in using a platinum crucible. In this proposed procedure, fifty milligrams of the powdered sample was placed in a PTFE bomb. To each sample was added 0.1 mL of HCl and 0.5 mL of HNO_3. The sealed bomb was then placed in an electric oven and heated to 150 °C for 3 h. After cooling, water was added to produce a final volume of 5 mL. After 5 min, the solution was used directly for the determination of nickel by GFAAS [9–13].

Experiment

Reagents and Standards

Ultra-high-purity water with a specific resistance of 18.2 MΩ cm from a Milli-Q Gradient water purification system (Millipore S.A.S., Molshem, France) and which has been filtered through a 0.22 μm membrane filter was used for all preparations and dilutions. All chemicals were of analytical grade. A standard solution of 50 ng/mL Ni was prepared daily by diluting a 1000 μg/mL atomic absorption stock solution (Specpure) with dilute nitric acid. Five working standard solutions with concentrations of 0.1, 0.5, 1.0, 5.0 and 10 ng/mL were prepared with the auto-sampler by taking different volumes of the standard solution. The acidity of the standard solutions was matched to that of the sample solutions.

Instrument

The measurements were carried out with an Analytik Jena (Jena, Germany) Model Zeenit 600 atomic absorption spectrometer with Zeeman effect background correction and a transversely heated graphite atomizer. A SSA6Z solid sampler device was used for the sample introduction. Hollow cathode lamps (VWR Scientific, cat. no. 58137-452, USA, for Ni) were used as line sources. Integrated contact tubes (Analytik Jena, part no. 407-152.013) and IC-Sample Platforms (Analytik Jena, part no. 407-152.023) were also used. The instrumental parameters of the spectrophotometer were as follows: wavelength at 232.0 nm and bandpass 0.2 nm. Pyrolytic graphite-coated graphite tubes were used. Argon (99.999%) gas was fluxed in the graphite tube. Peak height absorbance signals were measured by the instrument. The temperature program for the graphite tube is reported in Table 1.

Decomposition of Samples

Samples (50 mg) were placed in a PTFE digestion bomb [14] and 0.5 mL of a mixture of 1 volume of hydrochloric acid and 5 vol of nitric acid was added. This was allowed to digest at 150 °C for 5 h. Allowed to cool and the residue dissolved in water and diluted to 5.0 mL with the same solvent. After 5 min, the solution was determined directly by GFAAS.

Results and Discussion

Determination of Optimum Acid Conditions

Different combinations of the acid were used to decompose samples. The results are shown in Table 2. Based on these results, we concluded that HCl and HNO_3 provided the best acid combination. Next, we determined the optimal concentration of each acid. As shown in Table 2 the acid mixture of 1 vol of hydrochloric acid and 5 vol of nitric acid yielded the best results.

Determination of Heating Time

In order to determine optimal heating time, samples were decomposed under optimal acid conditions at 150 °C for periods of 1 to 8 h. As seen from Fig. 1, the samples were completely decomposed after 5 h.

Table 1 Heating program of the graphite furnace

Parameters	Dry			Pyrolysis			Atomization		
	I	II	III	I	II	III	I	II	III
Temperature (°C)	85	95	115	800	800	800	2100	2100	2100
Hold time (s)	5	40	10	5.0	1.0	2.0	1.3	2.0	2.0
Gas flow rate (L min^{-1})	3.0	3.0	3.0	3.0	3.0	0.0	0.0	0.0	0.0

Table 2 Activity of acid combinations

Sample ID[a]	Ni (μg g^{-1})		Experimental conditions (mL:mL)
	By our proposed method	By USP28/ EP2003	
HCO-080608	0.08	0.12	
HCO-080211	0.10	0.35	HNO_3
HCO-081121	0.32	0.68	
HCO-080608	0.10	0.12	
HCO-080211	0.21	0.35	$HNO_3/HCl = 6:1$
HCO-081121	0.54	0.68	
HCO-080608	0.13	0.12	
HCO-080211	0.35	0.35	$HNO_3/HCl = 5:1$
HCO-081121	0.72	0.68	
HCO-080608	0.11	0.12	
HCO-080211	0.29	0.35	$HNO_3/HCl = 3:1$
HCO-081121	0.59	0.68	
HCO-080608	0.09	0.12	
HCO-080211	0.18	0.35	$HNO_3/HCl = 1:1$
HCO-081121	0.34	0.68	
HCO-080608	0.06	0.12	
HCO-080211	0.11	0.35	$HNO_3/HCl = 1:3$
HCO-081121	0.24	0.68	
HCO-080608	0.06	0.12	
HCO-080211	0.08	0.35	$HNO_3/HCl = 1:5$
HCO-081121	0.11	0.68	
HCO-080608	0.02	0.12	
HCO-080211	0.03	0.35	HCl
HCO-081121	0.03	0.68	

The same substance was digested at 170 °C for 5 h

[a] The samples of the hydrogenated cottonseed oil were supplied by Xian-Janssen Pharmaceutical Ltd

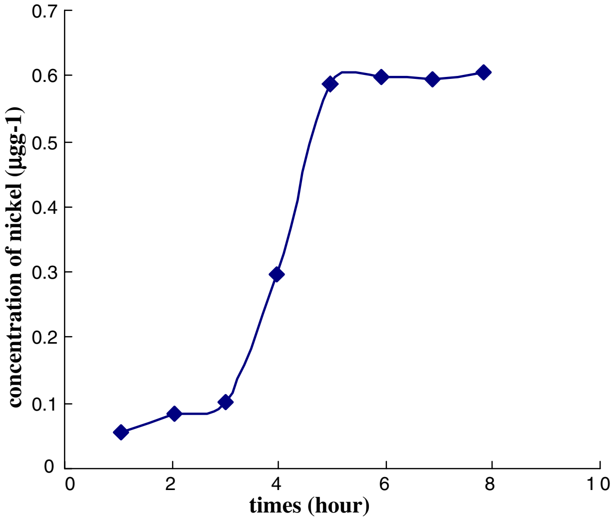

Fig. 1 Determination of heating times. The same substance was digested at 170 °C

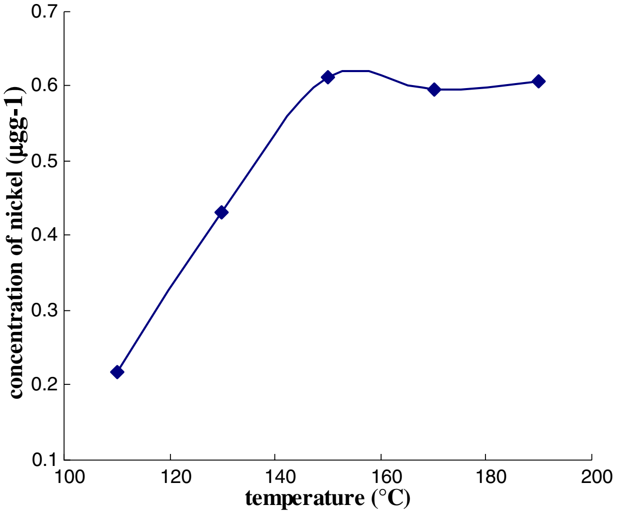

Fig. 2 Determination of heating temperature. The same substance was digested for 8 h

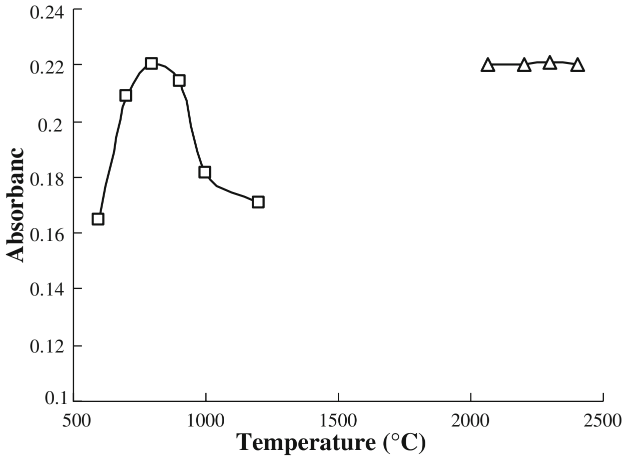

Fig. 3 Pyrolysis (*squares*) and atomization (*triangles*) curves of 0.2 ng Ni

Determination of Heating Temperature

To determine optimal heating temperature samples were decomposed under optimal acid conditions from 100 to 190 °C h for 8 h. As seen from Fig. 2, the samples were completely decomposed at temperatures above 150 °C.

Optimization of Pyrolysis and Atomization Temperature

The effect of pyrolysis and the atomization temperature on the analytical signal of 0.4 ng Ni both in aqueous solutions is shown in Fig. 3. The atomic signal for Ni diminished with pyrolysis temperatures above 900 °C in aqueous medium. The effect of the atomization temperature is

Table 3 Determination of nickel in hydrogenated cottonseed oil ($n = 5$)

Sample ID[a]	Ni ($\mu g\ g^{-1}$) By our proposed method	RSD (%)	By USP28/EP2003
HCO-080608	0.13	3.8	0.12
HCO-080318	0.26	3.4	0.24
HCO-080211	0.33	2.2	0.35
HCO-080509	0.56	1.8	0.59
HCO-081121	0.66	1.1	0.68
HCO-081022	0.77	0.8	0.79

The sample was digested at 150 °C for 5 h

[a] The hydrogenated cottonseed oil samples were supplied by Xian-Janssen Pharmaceutical Ltd

almost constant on the Ni analytical signal in aqueous matrices.

Characteristics of the Method

A series of standard solutions of nickel were detected by GFAAS. The absorption of Ni was proportional to the concentration of the acidified nickel in the range of from 0.2 to 10 ng/mL with a detection limit of 0.015 ng/mL. And the regression equation is $\mathrm{Abs} = 0.01221C_{\mathrm{nickel}} + 1 \times 10^{-5}$ and $r^2 = 0.9995$. The RSDs of five determinations were 3.6, 1.3 and 0.41% for 0.2, 1 and 5 ng/mL nickel, respectively.

Determination of Nickel in Hydrogenated Cottonseed Oil

Following the procedure detailed in Sect. 2, the proposed method was applied to the determination of nickel in hydrogenated cottonseed oil. The results are shown in Table 3. The content of nickel in hydrogenated cottonseed oil by proposed method was in agreement with the content determined using USP28/BP2003 with a platinum crucible.

Conclusion

The technique developed was practical and a pretreatment method avoiding tarnishing for the analysis of nickel in hydrogenated cottonseed oil.

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