Cloud point extraction – Flame atomic absorption spectrometry for the analysis of trace copper content in red bull sports drinks

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ABSTRACT

Taking the octyl polyethylene glycol phenyl (Triton X-100) as surface active agent, using diethyl dithiocarbamate sodium (DDTC) as complexing agent, we use Cloud Point Extraction—Flame Atomic Absorption Spectrometry (CPE-FAAS) to analysis the Cu(II) in the red bull sports drinks. In the best condition, by some experiment selections, such as pH value, heating time, equilibrium temperature, complexion agent concentration, surfactant concentration, interference ions, we got detection limit was 1.33ug/L, and RSD was 3.24% (n=11), the recoveries was between 97.20%~100.2%. The curve linear equation we used was $A = 6.6093C + 0.0438$, correlation coefficient was $r2=0.99668$, linear range was 200~1000ug/L.

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KEYWORDS

Cloud point extraction;
Flame atomic absorption spectrometry;
Copper;
Drinks.

INTRODUCTION

Copper is one of the essential elements for human health. It has some physiological function to hematopoietic cell growth, enzyme activity and human endocrine. Copper is useful for promoting blood circulation, improving central nervous system and the immune system, it is also important for hair, skin, bone tissue, the development of brain, liver and heart. Lack of copper can lead to osteoporosis fragile, skin lesions, and brain atrophy, ataxia, growth stagnation, lethargy, hair decolorizing and curly hair and disease, but excessive intake can cause a variety of diseases, such as hepatolenticular degeneration, idiopathic copper toxicosis, children intrahepatic cholestasis, etc. The World Health Organization advices, in order to maintain a health, adults should take in 0.03mg copper per day. The red bull has been developed from Thailand to the world. At the same time, it evolved into "sports" vitamin beverage from the general drinks, which made it be useful of promoting the body's metabolism, absorbing and decomposing sugar, quickly adding a lot of energy substances. The new drink can also regulate nervous system, which has remarkable efficacy on refreshing brain, replenishing physical strength and anti-fatigue. Therefore, when people being tired after sports, they can drink red bull to add energy, which can quickly eliminate the motion fatigue, inspire spirits, for which, the red bull is becoming the indispensable sports "drugs" improve performance. In sports, beverage preparation and reserve of Cu, Fe, similar to Zn, Mn, Ca and other trace elements will be absorbed in the movement process to maintain body balance, which is good for our body to add a certain amount of trace elements. To measurement the copper

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in red bull, we always use these methods, such as copper reagent method, graphite furnace atomic absorption spectrophotometry, flame atomic absorption spectrophotometry etc. Flame atomic absorption spectrophotometry is widely used for its rapid and accurate. The earliest use of cloud point extraction technology is by Hiroto Watanabe and Hiroaki Tanaka, they applied it in the determination of metal ions. This is a new environmental protection liquid—liquid extraction technology appeared in recent years. It does not use volatile organic solvents, does not affect the environment, but successfully be used in metal element separation and enrichment. We improved this method on the basis of integrated predecessors. We mainly used p-octyl polyethylene glycol phenyl ether (Triton X-100) as surface active agent, diethyl dithiocarbamate sodium (DDTC) as the complexion agent, and took the way of cloud point extraction—flame atomic absorption spectrum method to analysis trace copper, successfully measurement the trace copper content in red bull. This method is simple, rapid and accurate.

EXPERIMENT

Instruments and reagent

The used instruments are TAS-990 atomic absorption spectrophotometer (Beijing Purkinje General Instrument Limited Company), KJ-B oil free gas compressor (Tianjin Limay Hao Industry & Trade Limited Company), Copper hollow cathode lamp (KY-1, Beijing shuguangming electronic light source instrument Limited Company), Small high speed mill (WB-100 Beijing Weibohuang Mechanical Equipment Limited Company), 1/10000 AUY whole automatic analytical balance (Shimazu Japan) and 800B desk centrifuge (Shanghai Anting scientific instruments plant).

The purity of experiment reagent is PR. 1000g•L-1 copper reservior fluid is made With high purity copper by weighing. work solution (1x10-2g•L-1) was prepared with the upper solution. Triton X-100 was diluted to 1% (φ) solution, DDTC was made to 1x10-3mol•L- 1 spare solution, Boric acid solution and sodium borate solution are prepared PH9.0 buffer spare solution, It was Prepared that of 0.1 mol•L-1 nitric acid—ethanol spare solution, The experiment water are

secondary distilled water. All the containers were soaked with dilute nitric acid.

Experimental method

Sample preparation and processing

10.00ml sample solution six parts was respectively removed in 50ml clean beakers with glass-surface vessel which were numbered to be1~6. 15ml HNO3 + HClO4 (4+1) acid is mixed in upper six parts solution. Which were slowly heated to keep mirco boiling until they were colorless transparent. After glass-surface vessel and inner wall of beaker were flushed with 1% HNO3. They solution cooled to room temperature. The solution constant volume is 50.00mL with secondary distilled water. After they were sample and standard sample tested simultaneously.

Determination methods and working conditions of instrument

Determination of standard liquid. 0.2mL 1X10-2 g•L-1 copper standard liquid was accurately removed in centrifuge tube (10mL), in which 0.4mL Triton X-100 standard liquid, 0.3mL DDTC quasi liquid and 1mL PH 8.5 buffer solution were added with secondary distilled water constant volume was 10mL. Put in the 86°C constant temperature water bath 50min, it was centrifugated (3000r/min, 15min), it was put in ice water 4min, After its water phase was abandoned. 0.1mol•L-1 nitric acid—ethanol solution was added in the sample until constant volume was 2ml which was shaken up. The content of copper solution was determined FAAS in the solution. Working conditions of the instrument is that the detection optical wavelength is 283.0nm, Lamp current is 3mA, Spectrum bandpass is 0.2nm, Burner height is 6mm; and gas flow is1700 l/min.

RESULTS AND DISCUSSION

Surfactant Triton X-100 and complexing agent DDTC content on the effects of copper extraction rate

Measuring ion can be complex by a certain amount of complexing agent DDTC (as shown in Figure 1). When the dosage is between 0.2ml~0.4ml between, there is a maximum extraction rate, the experiment

chooses 0.3ml. The consumption of Triton X-100 directly affects the effect of separation, and the extraction efficiency. Therefore, in this experiment we put attention on the different results in the different dosage of Triton X–100 (Figure 2), and when it is 0.4mL, the extraction efficiency is the highest.
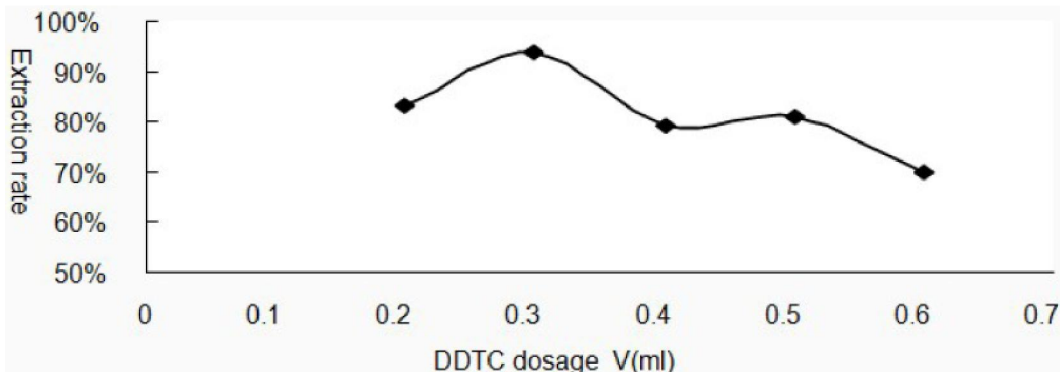

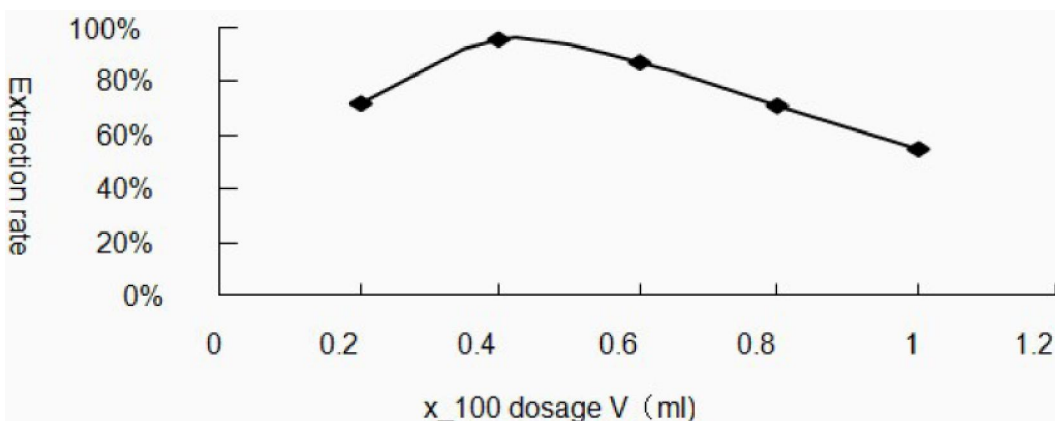**Figure 1 : DDTC - for the influence of extraction efficiency**

Figure 2 : X-100 - for the influence of extraction rate

The effects of pH value

pH value has certain effects on stability of metal ion formation. If the pH value is too low, the formation will be unstable; when it is too high, the extraction efficiency will be lower.

According to the test of different pH value, we got the result that when it was in the range of 7.5~9.5, the copper extraction effect was good. Therefore, 8.5 is best for the test (Figure 3).

The influence of equilibrium time and the temperature balance

Cloud point extraction was closely linked with balance time, equilibrium temperature, the two directly influence the extraction effect. For this reason, experiments were investigated 20min to 70min (as shown in Figure 4), 78°C~90°C (shown in Figure 5). The results showed that when the equilibrium time was 50min, extraction rate was maximum. When the equilibrium temperature is 86°C, the extraction efficiency achieved to the highest. When the temperature was too high or too low, equilibrium time was too long or too short, there will be different results. Therefore, in this experiment, 50min was the best equilibrium time, 86°C was the best equilibrium temperature.

The influence of centrifugal time and ice water bath time

If the centrifugal time is too long, it can lead to phase separation reversal, and the extraction efficiency will be lower. The test shows that there will be the highest extraction efficiency of 15min centrifugal, 4min ice water bath.

Coexisting ion interference test

In the chosen experimental conditions, we tested some general impacts of coexisting ions. They are listed in TABLE 1. The results show that the common ion

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Na+,Mg2 +, Fe3 +, Zn2 +, Mn2 +, K +, won't be influent on measurement of Cu2 +.
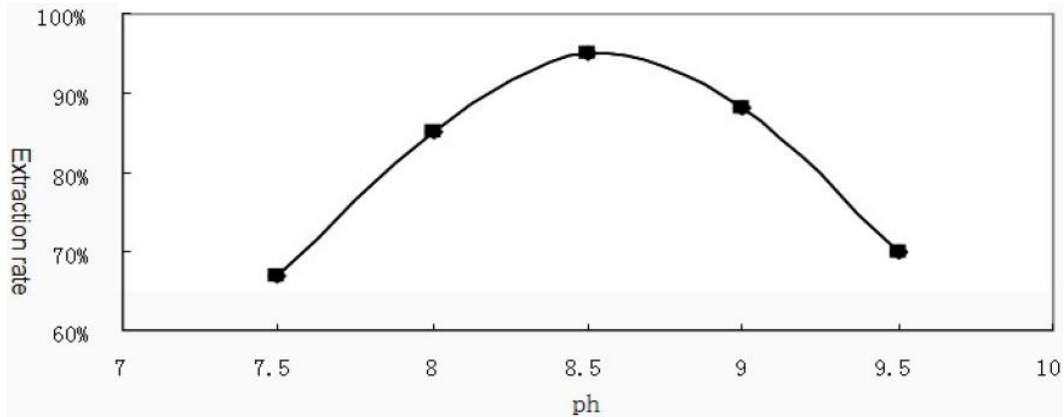

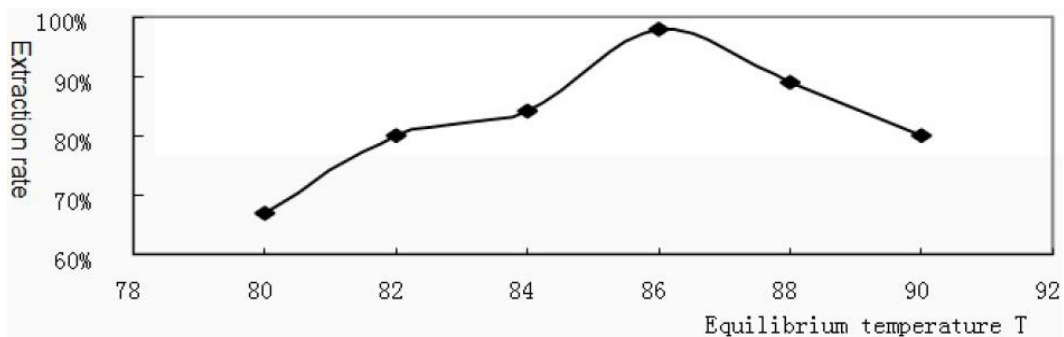**Figure 3 : pH - for the influence of extraction rate**

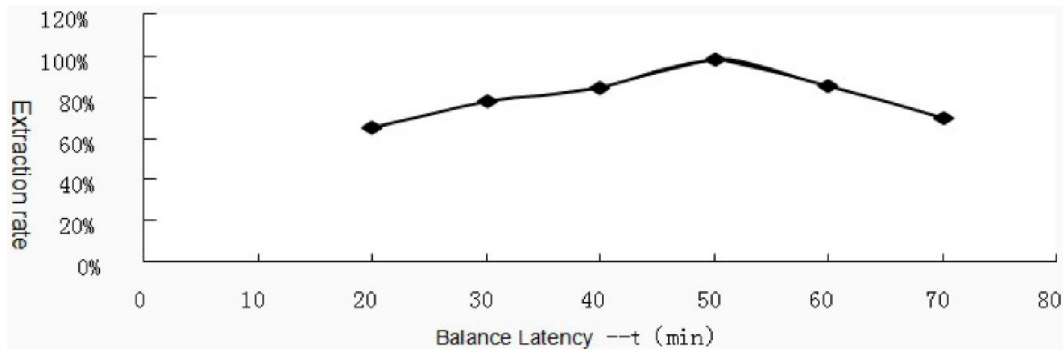**Figure 4 : Equilibrium temperature, for the influence of extraction efficiency**

Figure 5 : Equilibrium time - for the influence of extraction rate

TABLE 1 : Coexisting ion of interference

Coexisting ion	Tolerance multiples
Na+, K+ Fe3+	1500
Zn2+	100
Mg2+ Cr3+	500
Pb2+	50

THE TEST OF WORKING CURVE AND PRECISION

Under the selected and best experimental condi-

tions, we tested some parameters of the analysis method. The copper linear regression equation was A = 6.6093C+0.0438, and the results showed that there would be better linear (r2=0.99668) in the range of 200~1000ug/L, detection limit was 1.33ug/L, R SD was 3.24% (n =11).

ACTUAL SAMPLE MEASUREMENT AND RECOVERY

According to the experiment method to measure-

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ment and recover red bull drinks, we got the recovery rate is 97.20~100.2% (see TABLE 2), which show that the method is accurate.

TABLE 2 : Actual sample of copper measurement and recovery

Sample	Blank determination value (ug/g)	add scalar (ug)	Add scale Measured value (ug/g)	recovery (%)
Red bull 1	0.268	0.500	0.754	97.20
Red bull2	0.271	0.500	0.772	100.2
Red bull 3	0.270	0.500	0.767	99.40

CONCLUSION

Cloud point extraction is one of the useful ways to for the low-toxic, fast, simple and effective of the separation and enrichment of trace metal ions. It can form a stable complex in the buffer system of copper and DDTC in pH=8.5. Because of nitric acid, s reducing viscosity, and Triton X-100 is clound point characteristic. Triton X-100 is effective to separate and enrich Cu(II). It is simple, and the enriching rate is high. UsingA cloud point extraction treatment to take the samples, the result will be stable, the detection limit will be low. The test results are accurate and reliable, and meet the requirements of analysis. They are suitable for the quality control of red bull's production. And experimental analysis on copper content of the red bull is significant for the progress of sports performance and the fitness.

ACKNOWLEDGEMENTS

REFERENCES

[1] Baozhu Chen; Zhongtai red bull functional drinks brand creation research. Xiamen University Media Institute, 15-18 **(2009)**.

[2] Bing Zhang, Yan Feng; The special quality evaluation of the triple jump and the differential equation model of long jump mechanics based on gray correlation analysis. International Journal of Applied Mathematics and Statistics, **40(10)**, 136-143 **(2013)**.

[3] Cai Cui; Application of mathematical model for simulation of 100-meter race. International Journal of Applied Mathematics and Statistics, **42(12)**, 309-316 **(2013)**.

[4] Guo Dan; Graphite courtyard west search spectrophotometry commonly used oral liquid of trace element in the copper content. Drug of China, **2**, 110-111 **(2006)**.

[5] Haibin Wang, Shuye Yang; An analysis of hurdle performance prediction based on mechanical analysis and gray prediction model. International Journal of Applied Mathematics and Statistics, **39(9)**, 243-250 **(2013)**.

[6] Hongwei Yang; Evaluation model of physical fitness of young tennis athletes based on AHP-TOPSIS comprehensive evaluation. International Journal of Applied Mathematics and Statistics, **39(9)**, 188-195 **(2013)**.

[7] Liu Hong; In the purple Perilla leaf trace manganese catalytic kinetic photometry method. Food Science, **4**, 134-136 **(2004)**.

[8] Ming Cui Zhang; New fluorescent reagent 5-(4-fluorobenzene azo)-8-salicylic aldehyde shrinkage aminoquinoline fluorescence method determination of trace copper. Janalysis Laboratory, **3**, 13 -15 **(2005)**.

[9] Wan Shen Yao; Health treble - Zinc selenium copper. Health New Concept Life Care, **8**, 11-13 **(2008)**.

[10] Xia Shi Zhu; Cloud point extraction - Flame atomic absorption spectrometry determination of trace copper. Jspectrum Laboratory, **2**, 332-336 **(2005)**.

[11] Yu Gong Wang; Flame atomic absorption method direct determination of manganese in wine. Preventive Medicine BBS, **2**, 187-189 **(2006)**.