***MINERALOGIA**, 43, No 1-2: 137-146 (2012)*
DOI: 10.2478/v10002-012-0002-6
www.Mineralogia.pl

MINERALOGICAL SOCIETY OF POLAND
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Short note

Simple method of copper analysis using monosodium glutamate and its application in ore analysis

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Received: February 3, 2012
Received in revised form: April 20, 2012
Accepted: May 16, 2012
Available online: November 5, 2012

Abstract. A simple photometric method for copper (II) analysis using monosodium glutamate (MSG) is presented. The method is technically simple, inexpensive, quantitative, and makes use of readily available reagents. The rapid reaction of copper (II) with glutamate in aqueous solution at pH 10 to form a blue complex serves as a basis for the determination of copper (II) in the range of 10-500 µg/ml. Copper recovery is > 82%. The method could be used to determine copper (II) concentrations in iron ore samples.

Key-words: photometric determination, copper, monosodium glutamate

1. Introduction

Copper (Cu) is an element commonly analyzed in the laboratory as a part of many geological and mining studies. A variety of analytical methods copper is used, depending on the sensitivity, precision and accuracy required, the cost incurred and the time consumed. These methods include atomic absorption spectrometry (AAS), inductively coupled plasma spectrometry (ICP-Spectrometry) and spectrophotometry or photometry. AAS and ICP are generally preferred due to their sensitivity and simplicity, but involve a high capital cost (Moon et al. 2006). Photometry, widely applicable in trace-element analysis involves low capital cost and can be used in the field by relatively inexperienced operators (Jungreis 1997).

Photometric analysis depends heavily on special chemical reagents (chromogenic reagents) that react with the element concerned to produce differently colored compounds (Marczenko, Balcerzak 2000). For copper analysis, several chromogenic reagents are used, including dithizone (Butler Forbes 1965; Kumar et al. 1991), diethyldithiocarbamate (San Andres et al. 1994; Shah, Paul 1972; Ravnik et al. 1974), cuproine (Hoste et al. 1953; Irving, Tomlinson 1968; Larsen 1974), cuprizone (Peterson, Bollier 1955; Jacobsen et al. 1961) and 1,5-diphenylcarbazide (Stoner, Dasler 1960). However, analysis using these reagents is complicated and time consuming. Furthermore, they are expensive and not readily available.

A chemical compound which may address the problems of complicated procedure, cost and availability is monosodium glutamate (MSG). MSG, a sodium salt of glutamic acid, is readily available as a flavor enhancer with a relatively high (> 99%) purity. Glutamate is a naturally occurring non-essential amino acid (Ninomiya, 1998) which reacts with copper (II) in aqueous solution to form a blue complex (Fig. 1; Kállay et al. 2005; Hamada et al. 2009; Bastug et al. 2011; Bottari et al. 2001). This reaction could potentially be exploited in determining the copper content of an ore sample. In this paper, this possible application of MSG in the photometric determination of copper (II) content in geological samples is described and evaluated.

Fig. 1. Standard solutions used for calibration in photometric determination of copper. From left to right: 25, 50, 75, 100, 125, 150, 175 and 200 µg/ml copper (II).

2. Experimental

The chromogenic reagent employed in this experiment is MSG (>99%; Sasa brand produced by PT Sasa Gending Probolinggo, Indonesia. Copper (II) sulfate pentahydrate and sodium hydroxide (analytical grade) were produced by Merck. The apparatus used is a Spectroquant NOVA 60 spectrofotometer, including a 5 cm quartz cuvette and pH 0-14 universalindicator paper, all provided by Merck. Atomic absorption spectrometry to determine the copper content in ore samples was carried out in the Laboratory of Analytical

Chemistry, Department of Chemistry, Institute of Technology Bandung, Indonesia, using a Shimadzu AA-630 atomic absorption spectrophotometer.

A standard 1000 µg/ml solution of copper (II) was prepared by dissolving 3.928 g of copper (II) sulfate pentahydrate in 5 ml of concentrated sulfuric acid. The result was transferred to a 1 liter volumetric flask and diluted to mark with deionized water. Working solutions (standard solution and sample solution) were transferred into a 25 ml volumetric flask and pH adjusted to 9.5-10.5 by adding 5 M sodium hydroxide solution. As much as 2 ml of MSG 20% was then added to the flask and the mixture diluted to mark with deionized water and homogenized. The copper (II) content of the working solution was determined based on the absorbance as measured by the spectrophotometer at wavelength 605 nm. For higher concentrations, the copper (II) content could also be determined visually by matching the color of the sample solution with that of the calibrated standard solution.

Eleven iron ore samples containing copper were obtained from Iron Mining, Gunung Burhan, Tanjung Bintang, Lampung Selatan, Indonesia. Based on megascopic observation, the samples consisted of magnetite (Fe_3O_4) and hematite (Fe_2O_3) with a green crust of malachite ($Cu_2CO_3(OH)_2$) and a little silica (SiO_2). For analysis, the samples were comminuted to < 80 mesh particle size. About 0.2 grams was dissolved in a mixture of concentrated nitric acid and hydrochloric acid and heated to near dryness, leaving only silica and silicate. The results of the dissolution were filtered using Whatman 41 filter paper and the filtrate transferred to a 50 ml volumetric flask and diluted to mark with deionized water. About 2 ml of this diluted filtrate was used in each analysis.

3. The method: results and discussion

In order to determine the optimum wavelength at which absorbance was maximized, a standard solution was prepared. The solution contained 200 µg/ml copper (II) and 1.6 % glutamate concentration at pH 9.5. Absorbance measurements were performed at wavelengths ranging from 340-810 nm. The correlation between wavelength and absorbance (absorption spectra) of the copper (II)-glutamate (Cu-glu) complex is shown in Figure 2 with maximum absorbance at 605 nm. The pH has a considerable effect as the presence of protons in solution hinder complex formation as is shown by the decreasing color intensity at low pH. The blue color would reappear with addition of sodium hydroxide and excess glutamate added to guarantee the maximum color intensity (complex formation). Based on the experimental results, the optimum condition was attained at pH 9.5-10.5. At higher pH, the solution tended to be turbid due to copper hydroxides precipitation.

To study the effects of concentrations of MSG, a series of working solutions was made with copper (II) concentrations constant at 100µg/ml. Glutamate concentration in the working solutions was varied so that the molar ratio of glutamate/copper (II) ranged from 1-7. The relation between absorbance and molar ratio glutamate/copper (II) is shown in Figure 3; absorbance is positively correlated with the molar ratio up to molar ratio 5 and remains constant above that value. This indicates that the addition of MSG does not significantly affect the absorbance and that the molar ratio of Cu-glu complex in the working solution is 1:5. As Kállay et al. (2005), Hamada et al. (2009), Bastug et al. (2011)

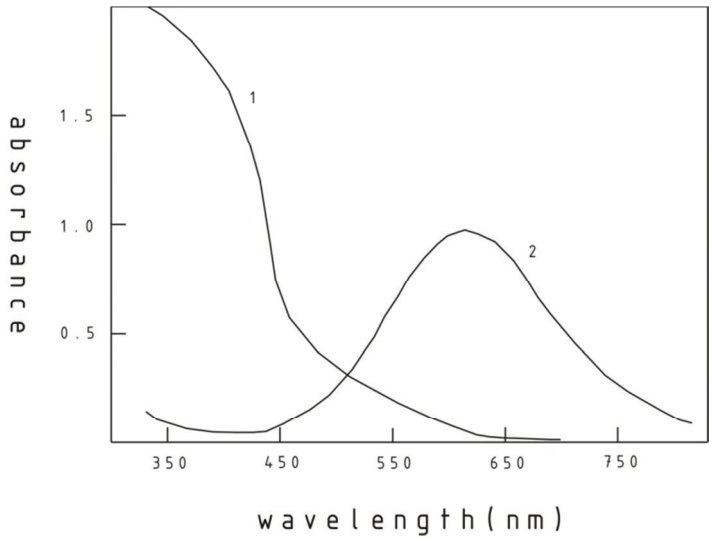

Fig. 2. 1 – absorption spectra of (1) iron (III)-glutamate complex, iron (III) concentration 500 µg/ml, pH 2 and MSG 1.6%. 2 – copper (II)-glutamate complex, copper concentration 200 µg/ml, pH 10, MSG 1.6%.

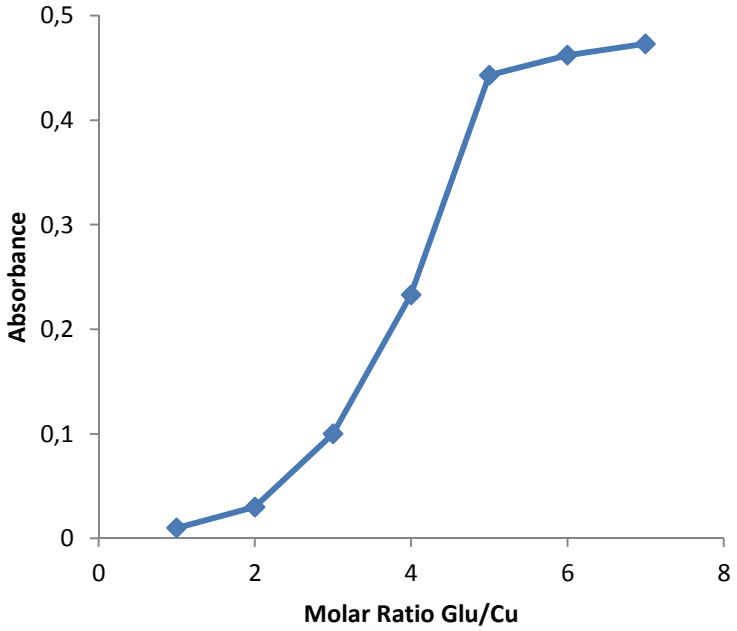

Fig. 3. Relation between absorbance and molar ratio of copper (II)-glutamate (Glu/Cu).

and Bottari et al. (2001) have shown, several species of Cu-glu complex with different molar ratios exist in aqueous solutions. Their existence depends on the pH of the solution and the deprotonation of the amide group of the glutamate. Kállay et al. (2005) stated that the carboxylate group is an important binding site to the copper (II) ion beside the amide group. UV/Vis spectrometry of the Cu-glu complex shows that the absorbance of the complex depends on the deprotonation of the amide group. A deprotonated amide group would form a complex of higher stability and more intense color as occurs at neutral- or basic pH. Glutamate with a deprotonated amide group would serve as a bidentate ligan and would form a complex with cupric ion with molar ratio 1:6 (Castro et al. 1995). The molar ratio 1:5 obtained from this experiment probably reflects incomplete deprotonation of the amide group of the glutamate (pH 9.5) since the optimum condition for deprotonation to form molar ratio 1:6 occurs at pH 11 (Kállay et al. 2005).

A calibration curve representing the association between absorbance and copper (II) concentration, required for copper (II) determination in sample solutions, was constructed using a series of standard (working) solutions with different copper (II) concentrations (Figure 4). The curve is linear and the correlation between absorbance and copper (II) concentration can be formulated using the linear regression equation A = 0.00467 C (µg/ml) + 0.024 with correlation coefficient r = 1.000, where A and C are absorbance and copper (II) concentration, respectively. The equation was confirmed for copper (II) concentrations falling in the range 10-500 µg/ml. At greater concentrations, the correlation loses its linearity. The lower concentration limit corresponds to the limit of detection.

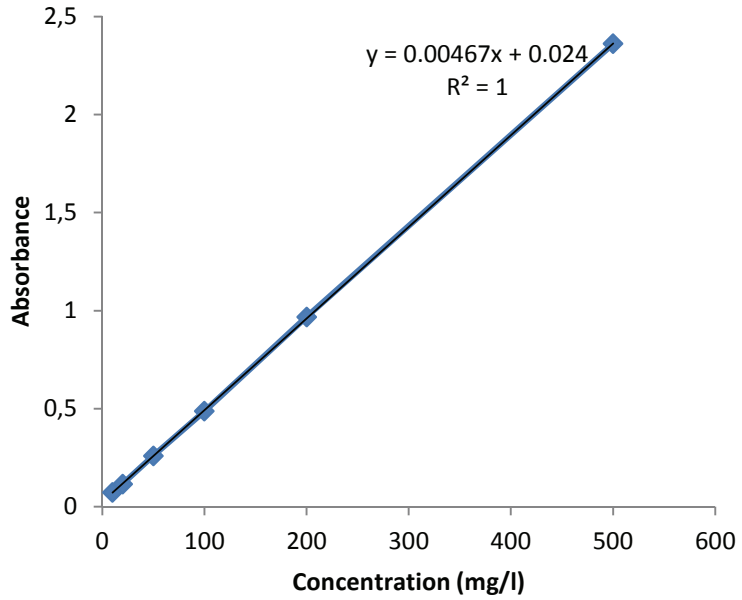

Fig. 4. Calibration curve for copper(II) concentration vs absorbance.

This photometric method has a theoretical detection limit of 1.3 µg/ml, assuming a lowest measured absorbance of ~ 0.030. The absorbance of the working solution could be measured at room temperature. Observation showed that a working solution of high concentration (≥ 100 mg/l) was stable for periods of at least 1 week. For more dilute solutions, observed instability with time was likely caused by sorption of ions from the flask surface (Al-Sibaai, Fogg 1973). However, differences in absorbencies for dilute 25 mg/l solutions, when re-measured after intervals of 1 hour, were negligible.

Evaluation of the possibility of error due to interfering ions in the determination remains qualitative. Iron (III) could cause interference by forming a brownish-red complex with glutamate. However, the likelihood of such interference is minimal as the absorbance of iron (III)-glutamate complex at wavelength 605 nm is negligible (Figure 2). In addition, formation of the complex can be prevented by adding sodium hydroxide to make the solution slightly more alkaline (pH 9.5 – 10.5). In such, iron (III) and many cations would be precipitated as hydroxides, leaving copper (II) in solution, chelated by glutamate. Decantation and filtration would separate any copper (II)-glutamate complex prior to absorbance measurement. Other ions including the alkaline metals K, Na, Mg and Ca, and transition metals Mn (II), Fe (II), Cr, Zn, Ca, Mg, Co and Ni have not been seen to form colored complexes with glutamate, but any such would tend to precipitate due to sodium hydroxide addition. Therefore, it is qualitatively concluded that these ions would not interfere in the determinations.

The method was successfully used to analyse the copper contents of eleven iron ore samples (section 2) collected from different sites in the same location. Four samples (Sample 01 – Sample 04) were used to determine accuracy and seven (Sample A-Sample G) to determine precision. All samples were subject to the treatment described in section 2. Some 2 ml of filtrate was transferred to 25 ml volumetric flask and the pH adjusted to 9.5-10.5 by addition of 5 M sodium hydroxide. 2 ml of MSG 20% solution was added and the mixture diluted to mark with deionized water and homogenized. Since the samples contained iron (III) which tend to precipitate at the optimum pH condition, filtration was used to separate Cu-glu complex as filtrate. The absorbance, at wavelegth 605 nm, of the filtrate was then measured. To determine the accuracy of the photometric determination, copper (II) contents were also determined by AAS; the results are summarized in Table 1.

TABLE 1

Determination of copper (II) in iron ore samples. Photometric (using MSG) and AAS results in µg/ml, recovery in % (photometric/AAS results).

No	Sample	Photometric	AAS	Recovery
1	Sample 01	122.698	123.957	98.98
2	Sample 02	38.543	46.322	83.21
3	Sample 03	38.544	46.753	82.44
4	Sample 04	46.895	45.376	103.35

Accuracy was estimated based on the recovery value (the best accuracy represented by 100% recovery). Based on the data on Table 1, the result of the photometric method using MSG as a chromogenic reagent had, for four samples, a recovery > 82% compared to AAS results which were deemed to be the true value. To assess the reproducibility (precision) of the photometric method, seven samples were each analyzed twice (Table 2). The results in Table 2 show that the deviation between two measurements for the same sample varied between 0.24-2.52%. The visual method (spot test), performed by comparing the color of a sample solution with the calibrated standard solution with known concentration (Figure 2), could be used only for semiquantitative determinations.

TABLE 2

Reproducibility of proposed MSG photometric method to determine copper concentrations after two measurements (MSG 1, MSG 2 in μg/ml). Diff. – difference between first and second measurement (in %).

No	Sample	MSG1	MSG2	Diff.
1	Sample A	43.897	44.218	0.73
2	Sample B	66.488	66.328	0.24
3	Sample C	51.499	51.017	0.94
4	Sample D	37.741	38.116	0.98
5	Sample E	38.812	39.722	2.29
6	Sample F	45.396	45.878	1.05
7	Sample G	37.259	38.223	2.52

Several methods for the photometric determination of copper are summarized in Table 3. These have been successfully used in analyzing copper contents in various types of samples including biological materials, foods, ground water, environmental samples, plants, wastes, alloys, sea water and crude oil. Only cuproine was cited in rock analysis (Marczenko, Balcerzak 2000). This is probably due to the selectivity of the reagent which is free of base-metal interferences, especially Pb, Zn, Cd and Fe. These metals are well known to associate with copper in rocks and ores (Moon et al. 2006). Methods with other reagents can be complicated and time consuming, requiring, e.g., sample pre-treatment (dithizone, dithiocarbamate, zincon, cuproine), slow reaction (cuprizone) and stabilizing agents (dithiocarbamate, 1-[pyridyl-(2)-azo]-naphthol). Pre-treatment can be required to separate copper from other interfering elements by solvent extraction or precipitation, or by a reduction process to convert divalent- into monovalent copper as with the cuproine method. Photometric determination using MSG as chromogenic reagents requires none of these processes. However the MSG method is less sensitive than other methods, suggesting that it might be most usefully applied in the analyses of ore samples with typical copper contents ranging from tens to thousands ppm (Moon et al. 2006, Laznicka 2006).

TABLE 3

Comparison of chromogenic reagents used in the spectrophotometric determination of copper.

No	Chromogenic reagent	Medium/solvent	λ max (nm)	Linear Range (μg/ml)	Interference	Reference	Remarks
1	dithizone	chloroform	550	0.03 - 80	Pt, Pd, Au, Ag and Hg	Butler and Forbes, 1965; Kumar et al. 1991	slow reaction, separation required
2	dithiocarbamate	chloroform	436	0.09 - 280	Fe, Bi, Mn, Ni, Co, Cr, Mo and U	San Andres et al., 1994; Shah and Paul, 1972; Ravnik et al., 1974	protective colloids, separation required
3	cuproine	isoamyl alcohol	546	0.2 - 600		Hoste et al. 1953; Irving and Tomlinson, 1968	reduction to Cu(I) required
4	cuprizone	aqueous	600	0.08 - 280	Ni, Co, Fe, Cr and U	Peterson and Bollier, 1955; Jacobsen et al., 1961	slow reaction
5	zincon	aqueous	600	0 - 2.6	Ni, Co and Zn	Ghasemi et al., 2003; Säbel et al., 2010	Ni and Zn separation required
6	1-[pyridyl-(2)-azo]-naphthol	chloroform	520	0.002 - 0.6	Zn, Cd	Thakur and Deb, 1999	TX-100 and N,N-diphenylbenzamidine required
7	monosodium glutamate	aqueous	605	1.3 - 500	-	this work	

4. Conclusions

Simple copper analysis may be carried out photometrically using monosodium glutamate. The method works for copper (II) concentrations in the range 10-500 µg/ml with a detection limit of 1.3 µg/ml. The method is a method for determining copper (II) contents in iron ore samples that is technically simple, quantitative, inexpensive, quantitative, and uses readily available reagents.

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