Monosodium glutamate for simple photometric iron analysis

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Abstract. Simple photometric method for iron analysis using monosodium glutamate (MSG) was proposed. The method could be used as an alternative method, which was technically simple, economic, quantitative, readily available, scientifically sound and environmental friendly. Rapid reaction of iron (III) with glutamate in sodium chloride-hydrochloric acid buffer (pH 2) to form red-brown complex was served as a basis in the photometric determination, which obeyed the range of iron (III) concentration 1.6 – 80 µg/ml. This method could be applied to determine iron concentration in soil with satisfactory results (accuracy and precision) compared to other photometric and atomic absorption spectrometry results.

1. Introduction
Iron (Fe) is one of the elements most frequently analyzed in laboratory for many different purposes or studies. For geological and mining studies, Fe analysis is executed using a variety of methods depending on the sensitivity or range of Fe content in the sample, precision and accuracy required, which is considering also the cost and time consumed in the analysis [1]. In geological studies, the Fe content in samples typically would be in the range from ppm to percent, although the most interest would be put in the range per mile and up [2, 3]. This is the case if the geological studies were conducted for prospecting and mining purposes.

In laboratory, the samples obtained from prospecting and mining (quality control) usually would be analyzed using atomic absorption spectrometer (AAS) or standard volumetric method, while samples obtained from geological studies would be analyzed using AAS or induced coupled plasma mass spectrometer (ICP-MS). AAS and ICP are generally preferred due to its sensitivity and simplicity, but notoriously sumptuous since they involved high capital cost. Other method used is photometry. This method has advantages in terms of versatility and sensitivity and even the sensitivity could compete with the sensitivity of AAS method. In geochemical and environmental studies, this method is still widely applicable to determine the trace element content in samples. The method has advantages since it involves low capital cost and could be executed directly in the field by a relatively inexperienced operator [4]. These advantages are considered significant due to the increasing interest in geochemical and environmental studies especially in poor and developing countries where the exploration program to find new mineral resources and the environmental problem are still of major concern. On the other hand, the increasing interest has to be balanced with the development of simple, quantitative, readily available, economic and scientifically sound analytical method [5].

The analysis cost in photometry directly depends on the special chemical reagents used (chromogenic reagent). For iron analysis, some of chromogenic reagents include thiocyanate [6, 7].
1,10-phenanthroline [8, 9] and bathophenanthroline [10]. Iron analysis using these chromogenic reagents has disadvantages due to its complicated procedure and very time consuming. Furthermore, in economic terms, these chromogenic reagents are expensive and not readily available. Besides, the application of these reagents could pose problems in disposal due to their toxic and non-biodegradable nature [11, 12].

One of chemical compound which could be proposed to address the problem of complicated procedure, economic factor, availability and disposal problem is monosodium glutamate (MSG). MSG is sodium salt of glutamic acid and easily obtained in market as flavour enhancer with relatively high purity (min. 99%). Glutamate could react with iron (III) in aqueous solution to form red-brown complex (Figure 1). This reaction further could be exploited as a basis in determining iron content in sample. Therefore in this paper the possibility of MSG application in photometric determination of iron (III) content would be discussed including the optimum condition, accuracy and reproducibility.

![Figure 1. Standard solution used for calibration in photometric determination of iron (III) from left to right: 20, 40, 60, 80, 100, 160 and 200 µg/ml iron (III)](image-url)

2. Experimental

2.1 Reagent and apparatus

The chromogenic reagent employed in this experiment is MSG (min. 99%), Ajinomoto brand, produced by PT Ajinomoto Indonesia. Powdered iron, 1,10-phenanthroline monohydrate, sodium chloride, nitric acid, sulfuric acid and hydrochloric acid were provided by Merck Chemical Indonesia all in analytical grade. The apparatus consists of Spectroquant NOVA 60 spectrophotometer, including 1 cm quartz cuvette, and pH 0-14 universal indicator paper, all provided by Merck Chemical. Atomic absorption spectrometry to determine the iron content in soil samples was carried out in Laboratory of Analytical Chemistry, Department of Chemistry, Institute of Technology Bandung, Indonesia using Shimadzu AA-630 atomic absorption spectrophotometer.

2.2 General procedures

Standard solution of iron (III) 1000 µg/ml was prepared by dissolving 1 g of dried iron powder in 5 ml of concentrated nitric acid and heated to nearly dryness. The result was then transferred to 1 liter volumetric flask and diluted to mark with deionised water. Working solutions (standard solution for calibration and sample solution) were made by transferred accordingly the standard solution of iron (III) or sample solution into 25 ml volumetric flask and buffered to pH 2 by adding 2 ml of NaCl/HCl buffer. MSG 20% was then added as much as 2 ml into the flask and finally the mixture was dilute to mark with deionised water. The iron (III) content of the working solution is determined based on
absorbance measured by spectrophotometer at wavelength 340 nm and 1 cm cuvette. Besides, the iron (III) content could be also determined visually by matching the colour of sample solution with the calibrated standard solution (figure 1).

2.3 Soil samples
The sample used in this study was soil samples obtained from coffee plantation Ranau area, West Lampung, Indonesia. The soil sample was dominated by silicate minerals (clay) and contained minor oxides. For analysis the soil samples were comminuted to less than 80 mesh particle size and as much as 0.2 gram would be destructed using mixture of concentrated nitric acid, hydrochloric acid and sulphuric acid and heated, leaving only silica and silicate. The destruction results were filtered using Whatman 41 filter paper and the filtrate were transferred to 50 ml volumetric flask and diluted to mark with deionised water. Further, as much as 2 ml of this diluted filtrate would be used in each analysis.

3. Results and discussions
In order to determine the optimum wavelength where the absorbance was maximum a working solution (standard solution for calibration) was prepared. The solution used contained 500 µg/ml iron (III) ion and 1.6 % glutamate concentration in final solution which was buffered with NaCl/HCl to pH 2. Absorbance measurement was performed in wavelength range 340 – 810 nm using spectrophotometer. The correlation between wavelength and absorbance (absorption spectra) of iron (III)-glutamate complex is shown in figure 2 which maximum absorbance occurred at 340 nm.

![Absorption spectra of iron (III)-glutamate complex](image)

**Figure 2.** Absorption spectra of (1) iron (III)-glutamate complex, iron (III) concentration 500 µg/ml, pH 2, MSG 1.6% (2) copper-glutamate complex, copper concentration 200 µg/ml, pH 10, MSG 1.6%

Acidity was significantly influenced the complex formation and its stability. Qualitatively it appeared that iron (III) ion would be precipitated as hydroxides if pH was greater than 3, marked by turbidity of working solution. At pH less than 2.5 and in extreme acid condition the complex would not be formed and colour intensity faded due to protonation of glutamate. In this case, pH 2 was chosen to avoid the precipitation of iron (III) ion and to cope with this problem, excess of glutamate was added to guarantee the maximum colour intensity.

To study the effects of concentrations of glutamate, a series of working solution was made which iron (III) concentration remained constant (200 µg/ml) at pH 2 using NaCl/HCl buffer. The glutamate/iron (III) molar concentration in working solution was varied between 1 and 13 (figure 3). The graph shows that absorbance is positively correlated with the molar ratio. This condition applied
until the molar ratio 1L while at the higher ratio the absorbance remained constant. This indicates that
the addition of more MSG do not affect the absorbance significantly and also indicates the molar ratio
of iron (III)-glutamate complex in working solution to be 1:11.

**Figure 3.** Relation between absorbance and molar ratio of glutamate/iron (III)

Calibration curve representing the association between absorbance and iron (III) concentration
was required for iron (III) determination in sample solution. The curve was constructed using series of
standard solution (working solution) with different iron (III) concentration (Figure 4). The curve was
linear and correlation between absorbance and iron (III) concentration could be formulated with linear
regression equation $A = 0.034c$ (µg/ml) – 0.031 with correlation coefficient $r^2 = 0.999$, where $A$ and $c$
stood for absorbance and iron (III) concentration respectively. The equation was conformed if iron
(III) concentration fell on the range of 1.6 – 80 µg/ml. For higher concentration the correlation of
absorbance – iron (III) concentration lost its linearity. Theoretically, if detection limit could be
calculated using the value of molar absorption and lowest measured absorbance ($≈ 0.020$) then the
concentration limit would be 1.47 µg/ml. The numerical value of sensitivity of proposed method, as
molar absorption coefficient ($\varepsilon$) and specific absorbance ($a$) were calculated to be $1.4 \times 10^3$ l.mol$^{-1}$.cm$^{-1}$
and 0.03 ml.µg$^{-1}$.cm$^{-1}$ respectively.

Working solution could be directly measured its absorbance immediately at room temperature.
Based on observation, a working solution was stable for at least 2 days, which was shown by
insignificance change in absorbance (decreasing less than 3% from initial absorbance). For higher
concentration range, linearity could be obtained using wavelength analysis 410 nm, within the range
10 – 200 µg/ml ($r^2 = 0.994$, concentration limit 2.43 µg/ml, $\varepsilon = 424$ l.mol$^{-1}$.cm$^{-1}$).

Observation on the possibility of interference by various ions as source of matrix error in this
determination was still qualitative. So far copper (II) or cupric ion caused interference by forming blue
coloured complex with glutamate. Absorption spectra of the complexes of iron (III)-glutamate is
shown in Figure 2. However, the interference of cupric ion could be minimized since based on the
Figure 2, the absorbance of cupric-glutamate complex in wavelength 340 nm was negligible. The
complex cupric-glutamate has a maximum absorbance at wavelength around 600nm. Besides, the
cupric-glutamate complex formation could be prevented in acidic solution (pH < 7). Other ions
including alkaline metals K, Na, Ca and Mg, and transition metals Mn (II), Fe (II), Cr, Zn, Co and Ni.
so far did not form coloured complex with glutamate, therefore, it is qualitatively indicated that these ions would not interfere in the iron (III) determination using MSG.

**Figure 4.** Calibration curve iron (III) concentration (c) – absorbance (A)

This proposed method was successfully applied in analysis of soil sample (section 2). The filtrate as much as 2 ml as result from destruction process was transferred to 25 ml volumetric flask and buffered to pH 2 by adding 2 ml NaCl/HCl buffer. MSG 20% solution was added as much as 2 ml into the flask and finally the mixture was dilute to mark with deionised water and homogenized. The absorbance could be directly measured at wavelength 340 nm using 1 cm cuvette. As comparisons, the same sample would be analyzed using standard photometric which 1, 10-phenanthroline was applied as chromogenic reagent. The procedure of the standard photometric determination referred to Marczenko and Balcerzak [13]. To determine the accuracy of both photometric determinations, iron (III) concentration in samples was also determined using atomic absorption spectrometer (AAS) which results were summarized in table 1.

**Tabel 1.** Determination of iron (III) in soil sample. Photometric and AAS results in µg/ml, recovery in % (ratio of photometric/AAS results). MSG and phen are proposed monosodium glutamate and standard 1,10 phenanthroline methods respectively

| No | Sample       | Photometric | AAS   | Accuracy |
|----|--------------|-------------|-------|----------|
|    |              | MSG        | phen  | MSG      | phen    |
| 1  | ER/01/SL     | 6.85       | 6.93  | 6.71     | 102.2   | 103.4   |
| 2  | ER/015/SL    | 5.85       | 6.03  | 6.21     | 94.3    | 97.1    |
| 3  | ER/022/SL    | 7.09       | 6.96  | 7.85     | 90.3    | 88.7    |
| 4  | ER/040/SL    | 5.62       | 5.52  | 6.11     | 91.9    | 90.3    |
| 5  | ER/054/SL    | 6.56       | 6.76  | 6.32     | 103.7   | 106.8   |
Based on table 1, the result of proposed photometric method using MSG as chromogenic reagent of 5 samples analyzed had accuracy between 90.32 % - 103.72 % compared to AAS results which were set as true value. These results even better than standard photometric method incorporated 1,10 phenanthroline which accuracy varied between 88.70 % - 106.83 % compared to AAS results. To assess the reproducibility (precision), five samples was analyzed twice using proposed method (table 2). Low RSD value (ratio between standard deviation and mean value), which is less than 5% signifies the high precision in analysis using proposed method.

Table 2. Reproducibility of proposed MSG photometric method to determine iron (III) concentration after two measurements (MSG 1 and MSG 2 in µg/ml)

| No | Sample   | MSG1 | MSG2 | RSD (%) |
|----|----------|------|------|---------|
| 1  | ER/028/SL| 4.74 | 4.68 | 0.89    |
| 2  | ER/038/SL| 4.59 | 4.71 | 1.80    |
| 3  | ER/051/SL| 7.15 | 7.27 | 1.16    |
| 4  | ER/053/SL| 6.06 | 6.18 | 1.35    |
| 5  | FK/068/SL| 13.50| 13.38| 0.62    |

4. Conclusions
Monosodium glutamate could be proposed as alternative chromogenic reagent in photometric determination of iron (III). Preconcentration and dilution could be carried out accordingly to meet the concentration range of 1.6 – 80 µg/ml with limit detection of 1.47 µg/ml. The proposed photometric method incorporating monosodium glutamate could be used as an alternative in determining iron (III) content in sample which is technically simple, quantitative, readily available, economic, scientifically sound and environmental friendly. This method is applicable to analyze iron content in soil sample with high accuracy and precision.

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