

## UV-Spectrophotometric Determination of 3-Glycidoxypropyltrimethoxysilane (GPTMS) and Epoxy Groups on GPTMS Modified Nanosilica

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A UV-spectrophotometric method has been developed for quantitative determination of 3-glycidoxypropyltrimethoxysilane (GPTMS) and epoxy groups on GPTMS modified nanosilica (GPTMS-SiO<sub>2</sub>). The procedure is based on the quantitative reaction of dihydroxyl of hydrated epoxy groups with potassium periodate to form iodate, which can be detected by UV-spectrophotometry, after being coloured using excessive iodide anion. The analysis of GPTMS and epoxy groups on GPTMS-SiO<sub>2</sub> yields results with favourable accuracy and reproducibility. Linearity has been obtained over the GPTMS (or epoxy groups) concentration range of  $2.2 \times 10^{-6}$ - $2.7 \times 10^{-5}$  mol L<sup>-1</sup> with r value of 0.9999. Influences of hydrolysis, oxidation and colouring conditions have also been investigated.

**Key Words:** Spectrometry, 3-Glycidoxypropyltrimethoxysilane, Nanosilica.

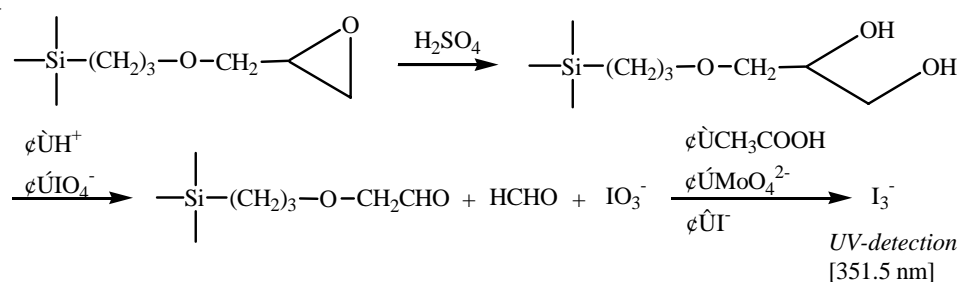
### INTRODUCTION

3-Glycidoxypropyltrimethoxysilane (GPTMS) and its modified nanosilica (GPTMS-SiO<sub>2</sub>) play a very important role as reactive intermediates for the solid phase synthesis<sup>1,2</sup> and covalent chromatography<sup>3</sup>, from analytical preconcentration to drug delivery and tissue engineering<sup>4</sup>. However, the quantitative determination of GPTMS and epoxy group on GPTMS-SiO<sub>2</sub> presents a number of difficulties with solution measurement. Some researchers applied GC method for detection of GPTMS<sup>5,6</sup>. However, they have not applied the method for detection of epoxy groups on surface GPTMS-SiO<sub>2</sub> owing to the solid nanosilica. There are many modern physical means to characterize GPTMS-SiO<sub>2</sub><sup>7-10</sup>, such as XPS, IGC, CP/MAS-NMR, FT-IR, TOF-SIMS, AFM, SEM and so on, but the testings are only qualitative or semi-quantitative analysis. The measurements of GPTMS and epoxy groups on surface GPTMS-SiO<sub>2</sub> by titration were also studied by Li *et al.*<sup>11</sup> and Radi *et al.*<sup>12</sup>. Li *et al.*<sup>11</sup> carried out the direct titration in non-aqueous phase and Radi *et al.*<sup>12</sup> followed by titrating the released hydroxyl coming from reaction of sodium thio-sulfate and GPTMS-SiO<sub>2</sub> with hydrochloric acid. The results suggested that these

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methods were suitable for GPTMS, while used for epoxy groups on surface GPTMS-SiO<sub>2</sub>, their end-points were not very clear because of the strong adsorption of soil vs. indicator.

In this study, a new method was developed for measurement of GPTMS and applied to measurement of epoxy groups on surface GPTMS-SiO<sub>2</sub>. The approach was based on (a) the quantitative hydrolysis of epoxy groups, (b) oxidation reaction between dihydroxyl and potassium periodate under weak acid condition, (c) colouring reaction between iodate ion which could be realised from surface of nanoparticles easily and (d) iodide ion in the presence of superfluous sodium molybdate which was used to shelter the remaining periodate ion. At the end triiodide ion was formed (**Scheme-I**). The triiodide ion can be measured by UV-spectrophotometer at 351.5 nm. The content of GPTMS and the amount of epoxy groups on surface GPTMS-SiO<sub>2</sub> were calculated accurately.



**Scheme-I:** Proposed reaction process of GPTMS or epoxy groups on surface GPTMS-SiO<sub>2</sub>

## EXPERIMENTAL

Reference GPTMS was obtained from J.K. Chemical Ltd. with the content of 97.2 %. Sample A was GPTMS which comes from Nanjing Compton Shuguang Organosilicon Chemical Co., Ltd. (China); Sample B, obtained from Henan province Nanomaterial Engineering and Technological Research Centre, was pilot GPTMS-SiO<sub>2</sub>. All the other reagents were of analytical grade.

**Preparation of reference:** GPTMS and sample A 4-10 mg reference GPTMS or samples A were treated with 15 mL 1.25 × 10<sup>-2</sup> mol L<sup>-1</sup> sulfuric acid at 75 °C for 40 min in 50 mL conical flask; after cooling, 3 mL 1 mol L<sup>-1</sup> hexamethylenetetramine and 2.0 mL 0.05 mol L<sup>-1</sup> potassium periodate were added respectively. The samples were kept for 25 min and were transferred into 50 mL volumetric flasks.

**Preparation of sample B:** 30-100 mg samples B were prepared with the same method as preparation of reference GPTMS or sample A. The soil particles were washed with high purity water for 3 times and eliminated by centrifugation. Amalgamate all supernatant liquors to 50 mL volumetric flasks.

**Method:** Different volumes of prepared solution of reference GPTMS, samples A or B were put into 25 mL colourimetric tube. After the additions of 3.0 mL 0.04 mol L<sup>-1</sup> sodium molybdate, 2.5 mL 0.048 mol L<sup>-1</sup> acetic acid and 3.0 mL 0.04 mol

L<sup>-1</sup> potassium iodide, the mixtures were kept in dark for 25 min and then were diluted to volume and detected at 351.5 nm by UV-spectrophotometer. All the samples should be detected with the reagent blank as references.

## RESULTS AND DISCUSSION

**Temperature and time influencing hydrolysis of sample:** When the samples were treated with sulfuric acid, temperature and time had very important impacts on the results (Figs. 1 and 2). A lower temperature or a shorter time can lead to the incomplete hydrolysis reaction, while a higher temperature or a longer time can make the formed dihydroxyl dehydrated. During the process of experiment, 75 °C and 40 min were controlled strictly.

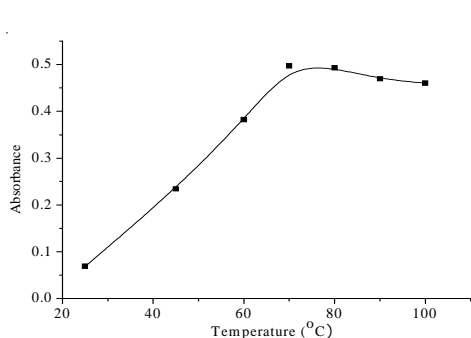


Fig. 1. Influence of hydrolysis temperature

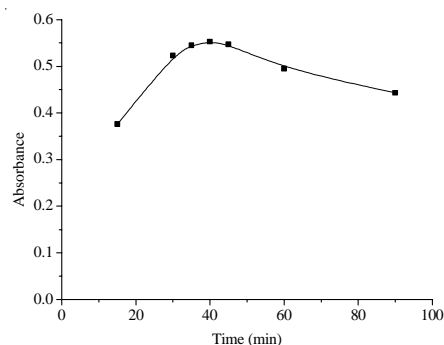


Fig. 2. Influence of hydrolysis time

**pH and addition of potassium periodate influencing oxidation reaction:** pH and addition of potassium periodate could have major impacts on the results (Figs. 3 and 4).

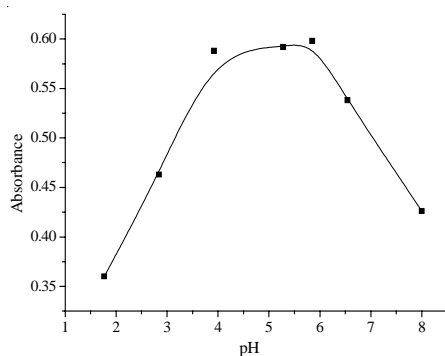


Fig. 3. Influence of pH

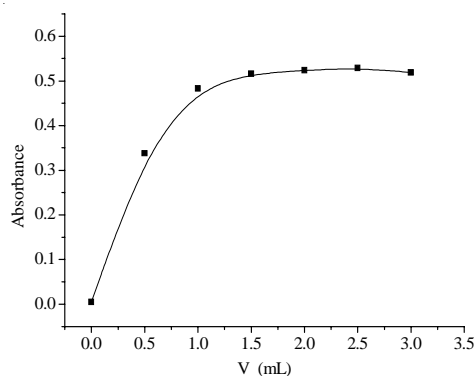
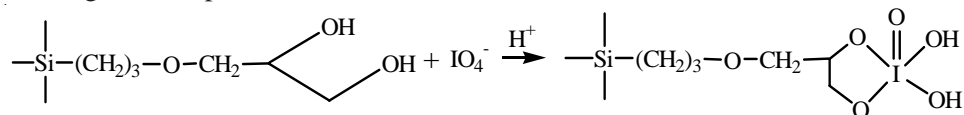


Fig. 4. Influence of addition of potassium periodate

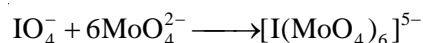
Generally process of periodate acid oxidating dihydroxyl is carried out *via* forming circular periodate acid-ester:



pH could influence the existing form of periodate ion and reaction rate. At a lower pH, periodate ion may exist mainly as  $\text{H}_5\text{IO}_6$  which would decrease oxidation reaction rate, while a higher pH is not favourable for the process of oxidation reaction. Furthermore, the reduction product iodate ion and the oxidation product formaldehyde can react in alkaline conditions, which may also affect the results. Fig. 5 showed that pH should be controlled in between 4.5-6.2. Based on the above work, buffers of  $\text{CH}_3\text{COOH-CH}_3\text{COONa}$ ,  $\text{KH}_2\text{PO}_4\text{-K}_2\text{HPO}_4$  and hexamethylenetetramine were attempted to experiment. It indicated that the former two had influence on the results, whereas the latter didn't and the reproducibility was good. 3 mL ( $1 \text{ mol L}^{-1}$ ) hexamethylenetetramine was selected during the process of experiment and then pH was 5.4-5.6.

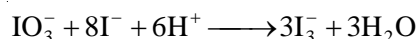
Fig. 4 described the influence of addition of potassium periodate, indicating that the oxidation would react completely when the addition of 0.05 mol/L potassium periodate was more than 1.5 mL. It can be that calculated that the addition of potassium periodate was twice more than that of original GPTMS (or amount of epoxy groups) when the oxidation can react completely. More than 2.5 times was confirmed during the procedure.

**Addition of sodium molybdate and potassium iodide influencing colouring reaction:** Sodium molybdate was mainly used to shelter the surplus periodate ion. The reaction is as follows:



This reaction must be carried out in acidic medium whose pH was more than 2.0<sup>13</sup>. During the process of experiment, 2.5 mL  $0.5 \text{ mol L}^{-1}$  acetic acid was added and pH range was 2.9-3.1. The addition of sodium molybdate was also very important. The experimental results indicated that the influence of excess periodate ion could be eliminated completely, when the mass of sodium molybdate was 150 times more than that of the excess periodate ion.

The addition of potassium iodide was another important factor which influenced the colouring reaction. Under acidic circumstance, it reacted with iodate ion and formed triiodide ion as follows:



This reaction must be carried out in dark or else the triiodide ion could not be gained. It showed that when the amount of potassium iodide was 120 times more than that of iodate ion, iodate ion could transfer into triiodide ion completely during the process of experiment.

**Linearity:** Reference GPTMS calibration solution were prepared and detected. The linearity was obtained over the GPTMS (or epoxy groups) concentration range  $2.2 \times 10^{-6}$ – $2.7 \times 10^{-5}$  mol L<sup>-1</sup> (Fig. 5) with the calibration curve following as:  $A_{351.5\text{nm}} = 5.07 \times 10^4 c + 0.00926$  ( $r = 0.9999$ ,  $n = 7$ ).

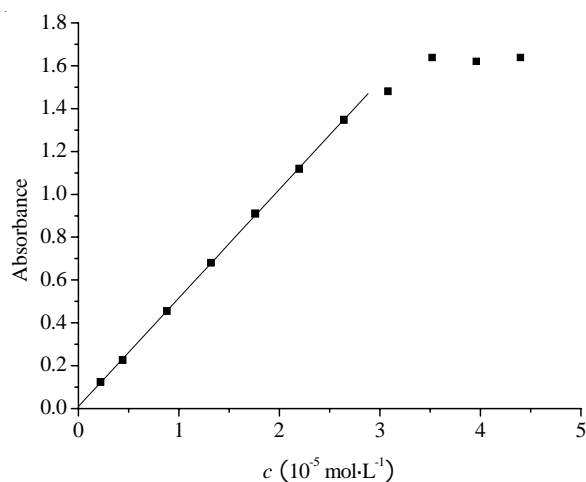


Fig. 5. Absorbance vs. concentration of GPTMS

**Determination of A and B:** According to the method, samples A and B were determined respectively. The content of sample A and epoxy groups of sample B were shown in Table-1.

TABLE-1  
DETERMINATION OF SAMPLE A AND B

Samples	Values of determination					Average
A (%)	98.83	99.23	99.35	99.62	98.71	99.15
B (mmol/g)	0.5562	0.5474	0.5385	0.5455	0.5483	0.5472

**Recovery of reference GPTMS:** In this text, recovery of GPTMS added in sample A or B were determined for evaluating the accuracy of the method. The results (Table-2), indicated that the method's accuracy is satisfactory.

TABLE-2  
RECOVERY RATES OF REFERENCE GPTMS IN SAMPLES A AND B

No.	Recovery rate					Average	Standard deviation
GPTMS in A (%)	101.7	100.5	102.3	99.06	99.21	100.6	1.45
GPTMS in B (%)	98.81	96.24	103.8	97.88	101.0	99.55	2.94

**Interference test:** Various interference, which may be existing in samples, were investigated by comparing the reference GPTMS solution to the reference GPTMS solution which were added interference. Considered the deviation is less

than 5 %, results showed that, when the mass ratio (mass of interference : mass of reference) is 1000, interference such as methanol, ethanol, acetic acid and silica with centrifugation eliminated, did not disturb the determination, but acetone, dioxane, DMSO and silica (50) without centrifugation eliminated can affect the determination considerably.

### Conclusion

In this work, a sensitive UV-spectrophotometric method has been developed for quantitative measurement of GPTMS and epoxy groups on surface GPTMS modified nanosilica. Influences of hydrolysis, oxidation and colouring conditions have also been discussed. Results indicated that the method provided with good parallelism and accuracy. It can be used to determine the content of GPTMS and the amount of epoxy groups on surface GPTMS-SiO<sub>2</sub> and other correlation products. It provides more technical support on development and application of GPTMS and its modified silica is of great importance.

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