Embedment of Cr(Ⅵ) by Alkoxide-Gel

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Osmic acid (2 to 4% solution of OsO₄) has been used for a long time as a fixing reagent of bio-specimens for electron microscopy. The treatment procedure of waste osmic acid has not yet been established due to its harmful effect. This note describes a technique to stabilize chromic acid as a substitute for osmic acid by alkoxide-gel formation. [Received December 21, 1985]

Key-words: CrO₃, OsO₄, Electron microscope, Alkoxide-gel, Embedment

1. Introduction

In this study, the embedment procedure is divided into two stages in order to make the embedding more stable. The first stage is the embedment by alkoxide-gel, a person making bio-specimens for observation by an electron microscope, a discharger of the waste fluids, conducts in his laboratory. The second stage is the embedment by low-melting glass a treatment expert carries out in a disposal plant of experimental waste to make the alkoxide-gel embedding much more stable.

This note will state the informations obtained in making experiments on the embedment by alkoxide-gel, the first stage.

2. Experiments

The variable factors and each corresponding value were setted and conditional experiments were made. The optimum conditions were determined by using an orthogonal array and confirmatory experiments were carried out according to the optimum conditions obtained. Results alone of confirmatory experiments are reported here.

The embedment effects were represented in terms of percentage of the entire eluted total chromium.

The concentration of total chromium in the eluate was measured by atomic absorption spectrophotometry.

2.1 Chemicals used

4% CrO₃ solution was employed as an original solution, Si(OC₂H₅)₄ and C₂H₅OH as gel materials, NH₂OH·HCl as a reducing agent, and NaOH was used as a gel accelerating agent depending upon the case.

2.2 Procedures of experiments

Gel materials in a fixed amount were placed in a 100ml of beaker, to which an original solution in a fixed amount was added. After a mixture was stirred with a stirrer, a reducing agent in a stated quantity was added to the mixture and it was stirred further. It was allowed to stand at room temperature for one to four days in case of non-caustic gelation, but 40% NaOH solution in a fixed quantity was added to it in case of caustic gelation. Both gels were subsequently dried with a drier at 100° to 105°C for 1 h and treated as a specimen.

2.3 Determination procedure

One gram of accurately weighted dry gel was put into 10 ml of HCl aqueous solution controlled its pH to 6.0 and were shaked for half-hour. Shaking condition was an oscillation of 45 to 50 mm and about 200 times/minute.

After the pH of an eluate was measured, the eluate was filtered with GFP (1 μm), washed with distilled water, adding 1ml of HCl (1+1), and made a total of 50 ml by adding distilled water. After testing whether or not Cr (Ⅵ) was
included in the eluate by use of diphenylcarbazide test paper, the total chromium concentration in the eluate was measured by atomic absorptiometric method,

\[
\frac{\text{eluted total chromium}}{\text{chromium content}} \times 100 = \text{percentage of eluted total chromium (\%)}
\]

was determined.

3. Results

3.1 In case of non-caustic gelation

Setting conditions (mixing ratio)

\[
\begin{align*}
\text{Si(OCH}_3\text{H}_4)_4 & \quad 5, 10, 15(\text{ml}) \\
\text{C}_2\text{H}_5\text{OH} & \quad 2, 5, 10(\text{ml}) \\
\text{NH}_2\text{OH-HCl} & \quad 0.2, 0.5, 0.8(\text{g})
\end{align*}
\]

3.2 In case of caustic gelation

Setting conditions (mixing ratio)

\[
\begin{align*}
\text{Si(OCH}_3\text{H}_4)_4 & \quad 5, 10, 15(\text{ml}) \\
\text{C}_2\text{H}_5\text{OH} & \quad 2, 5, 10(\text{ml}) \\
\text{NH}_2\text{OH-HCl} & \quad 0.2, 0.5, 0.8(\text{g})
\end{align*}
\]

3.3 Stabilities of non-caustic and caustic gels

According to the mixing ratio of No.1 in Table 1 and No.2 in Table 2, 37.5 ml of an original solution of 4% CrO3 solution was gelled. This study examined the chemical and thermal stabilities of the resultant non-caustic and caustic gels.

Tables 3 and 4 showed the results in terms of percentage of eluted total chromium (%).

4. Conclusion and discussion

4.1 In case of non-caustic gelation

When the volume ratio of Si(OCH3H4)4/C2H5OH was 2.0 or more, the non-caustic gel with low percentage of eluted total chromium could be made.

A reducing agent, 0.2 g of NH2OH · HCl, was enough to enable reduction of 2.5 ml of the

| Table 1. The optimum conditions of non-caustic gelation and results of the confirmatory tests (2.5 ml of 4% CrO3 solution was used as an original solution). |
|---|---|---|---|---|---|---|---|
| Si(OCH3H4)4 | C2H5OH | NH2OH·HCl | gelation time | yield | pH of eluate | total Cr conc. in eluate | percentage of eluted total Cr |
| (ml) | (ml) | (g) | (day) | (g) | (day) | (ppm) | (%) |
| 1 | 5 | 2 | 0.2 | 1 | 1.65 | 1.8 | 0.95 | 0.03 |
| 2 | 10 | 2 | 0.2 | 2 | 3.38 | 2.2 | 0.50 | 0.03 |

| Table 2. The optimum conditions of caustic gelation and results of the confirmatory tests (2.5 ml of 4% CrO3 solution was used as an original solution). |
|---|---|---|---|---|---|---|---|
| Si(OCH3H4)4 | C2H5OH | NH2OH·HCl | 40%NaOH | yield | pH of eluate | total Cr conc. in eluate | percentage of eluted total Cr |
| (ml) | (ml) | (g) | (ml) | (g) | (day) | (day) | (ppm) | (%) |
| 1 | 10 | 5 | 0.5 | 2 | 3.65 | 11.5 | 1.25 | 0.09 |
| 2 | 10 | 10 | 0.8 | 2 | 3.86 | 9.8 | 0.85 | 0.05 |

| Table 3. Chemical stabilities of non-caustic and caustic gels. |
|---|---|---|---|---|---|
| pH | 2.0 | 4.0 | 6.0 | 8.0 | 10.0 | 12.0 |
| Non-caustic gel | 0.12 | 0.13 | 0.12 | 0.12 | 0.13 | 0.12 |
| Caustic gel | 0.14 | 0.15 | 0.14 | 0.14 | 0.14 | 0.14 |

(HCl and NaOH were used for control of the pH.)

| Table 4 Thermal stabilities of non-caustic and caustic gels. |
|---|---|---|---|---|---|---|
| Temp. (°C) | room temp. | 200 | 400 | 600 | 800 | 1000 |
| Non-caustic gel | 0.12 | 0.003 | 0.05 | 0.08 | 0.01 | 0.01 |
| Caustic gel | 0.14 | 1.81 | 19.2 | 32.3 | 48.5 | 46.7 |

(Both gels were heated in the air for 2 hrs.)
original solution of 4% CrO₃ solution.

4.2 In case of caustic gelation

Although the caustic gel had an advantage that gelation has completed in a moment, the percentage of eluted total chromium was slightly inferior to that of the non-caustic.

4.3 Stability

As far as HCl and NaOH were used for controlling pH, chemical stability tests of both gels gave good results judging to be stable.

In experiments of heating stability in the air, the non-caustic gel was decreasing in the percentage of eluted total chromium and became stable as elevated temperature, while the caustic gel was increasing in the percentage by slight heating, resulting in its remarkably damaged stability.

Differential thermal analysis of non-caustic and caustic gels is illustrated in Fig. 1.

Both gels had a heating at 340°C to 370°C considered by combustion of residual Si(OC₂H₅)₄ after dehydration of adhering water.

![Fig. 1. DTA of non-caustic and caustic gels.](image-url)