Magnetic graphene oxide as sorbent for SPE of melamine from water

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Abstract. Melamine introduced into environment water through various industrial effluents can pose negative effects on ecosystem, thus it is required to establish suitable analytical methods for detection of melamine in environmental water samples. In this work, magnetic graphene oxide was synthesized and used as the sorbent for solid phase extraction (SPE) of melamine. The parameters that affect the extraction efficiency of melamine were studied. The optimum conditions, including sample pH, extraction and desorption time, and eluent volume were obtained. The analytical performance of the method was evaluated, and it was found that the limit of detection for melamine was 0.15 μg/L and the relative standard deviation was 3.6 %. The proposed method was utilized in the detection of melamine in various water samples with recoveries of 92.0-95.8%.

1. Introduction
Melamine (1, 3, 5-triazine-2, 4, 6-triamine, C₃H₆N₆) has been produced in large amounts. Melamine-contaminated infant formulas have resulted in serious health problems [1-3]. Nowadays, melamine has also been present in the environment as a result of its widespread uses [4-6]. Consequently, it is necessary to develop suitable analytical methods for determination of melamine in environmental samples. Because melamine in environmental water samples is often at low levels, suitable sample preparation procedures are often needed before its determination. Among various sample preparation techniques for trace analysis, solid phase extraction (SPE) is the most often used one and has achieved satisfactory results [7-18].

Graphene oxide (GO) is the oxidized derivative of graphene, which has an ultrahigh-specific surface area, superior chemical property and physical stability. Thus, GO can be used as sorbent materials for SPE [19-29].

Traditional SPE is always a tedious process. However, magnetically separation technology can provide an easy and rapid way for separation of magnetic particles from solution by applying a magnetic field [30-36].

In this work, magnetic graphene oxide (MGO) was prepared, and applied for SPE of melamine from aqueous solution. The parameters that affect the extraction efficiency of melamine were investigated, including sample pH, extraction time and desorption time, and eluent volume. The analytical performance of the method was examined. Finally, the developed method was applied for the determination of melamine in environmental water samples, and satisfactory analytical results were acquired.

2. Materials and methods
2.1. Chemicals
Melamine (>99.9%) was obtained from Aladdin Reagent (Shanghai) Co., Ltd (Shanghai, China). Nature graphite powder (99.95%) was purchased from Sinopharm Chemical Reagent Co., Ltd (Shanghai, China). Other chemicals and materials were purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China).

2.2. Apparatus
A HPLC system (SHIMADZU, Kyoto, Japan) equipped with diode array detection (DAD, SPD-M20A) and a Shim-pack VP-ODS column (150 × 4.6 mm I.D.) was utilized for analysis.

2.3. Preparation of MGO
Graphite oxide (GO) was prepared from nature graphite powders by a modified Hummers method, and magnetic graphite oxide (MGO) was synthesized by a one-pot solvothermal reaction [19].

2.4. Solid phase extraction
50 mg of MGO was added to the 200 mL melamine containing water sample, and the solution pH was adjusted to pH 6. After shaking for 20 min, the MGO was separated from solution using a magnet. The adsorbed melamine was eluted with 3 mL of 6% ammonia-methanol solution.

3. Results and discussion

3.1. Selection of sample pH
The influence of pH of aqueous solution on the extraction efficiency of melamine was explored by varying pH value from 3 to 10. As shown in Fig. 1, the recovery increased with the increase of pH from 3 to 5, and then dropped slightly up to 8. When the pH value was larger than 9, the recovery decreased significantly. Therefore, pH 6 was selected.

![Figure 1. Effect of solution pH.](image)

3.2. Selection of extraction time
The effect of extraction time on extraction efficiency of melamine was investigated. As can be seen from Fig. 2, the recovery increased drastically at the initial adsorption stage from 1 to 10 min. After 20 min, the recovery showed very little changes since the sorption equilibrium was achieved. Based on these results, 10 min was employed as the optimal extraction time.
3.3. Selection of eluent volume
In this study, 6% ammonia-methanol solution was used as the eluent for stripping of melamine from the MGO. To examine the effect of eluent volume on the extraction recovery of melamine, different volumes of the eluent (1, 2, 3, 5, 8 and 10 mL) were tested. The results showed that 3 mL of this solution could efficiently elute the adsorbed melamine.

3.4. Selection of desorption time
In order to investigate the optimum desorption time, various time periods were examined in the range of 1 to 20 min. The results were shown in Fig.3. According to Fig.3, 5 min was found to be sufficient for quantitative elution of melamine from MGO.

![Figure 2. Effect of extraction time.](image)

![Figure 3. Effect of desorption time.](image)
3.5 Analytical performance
Under the optimum experimental conditions, the calibration curve of melamine was linear in the concentration range from 0.3 to 30 (R² = 0.9956). The limit of detection (LOD) were 0.15 µg/L. The relative standard deviation (RSD) for 5 replicate measurements of 2.0 µg/L melamine was 3.6%.

3.6. Water sample analysis
To evaluate the capability of the proposed method for analysis of real samples with different matrices containing various amounts of melamine, three environmental water samples were analyzed, and the analytical results were given in Table 1.

Table 1. Analytical results of melamine in water samples.

| Sample          | Add/ (µg/L) | Found/ (µg/L) | Recovery (%) | RSD (%) |
|-----------------|-------------|---------------|--------------|---------|
| Water sample 1  | 0           | ---           | ---          | 4.2     |
|                 | 1.0         | 0.92          | 92.0         | 3.3     |
| Water sample 2  | 0           | 8.65          | ---          | 3.5     |
|                 | 10.0        | 17.98         | 93.3         | 2.1     |
| Water sample 3  | 0           | 65.42         | ---          | 1.2     |
|                 | 50.0        | 113.3         | 95.8         | 2.6     |

4. Conclusions
This study developed a new method for determination of melamine in aqueous solution, using MGO based SPE coupled with HPLC-DAD. The adsorption results obtained from this study suggest that the prepared MGO can act as a suitable sorbent for melamine. Recoveries of melamine were in the range of 92–95.8% with RSDs of 1.2–4.2%, showing the practicability of the proposed technique.

5. References
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