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On-line monitoring trihalomethanes in chlorinated water by membrane introduction–fast gas chromatography mass–spectrometry

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Abstract

An analytical method based on membrane introduction and fast gas chromatography–mass spectrometry (GC–MS) has been developed for the on-line monitoring of trihalomethanes (THMs) in chlorinated drinking water. The coupling of membrane introduction with fast GC–MS offers the advantage of membrane introduction as an on-line sampling device and fast GC–MS as a separation and identification method. While maintaining the on-line monitoring characteristic of traditional membrane introduction mass spectrometry (MIMS), the difficulty of distinguishing CHCl_3 and CHBrCl_2 in MIMS was overcome by rapid GC separation and MS analysis. Water permeated across the membrane affected the analysis of CHBr_2Cl and CHBr_3 . A method based on controlling the injection temperature and injection time has been developed to overcome the moisture problem. This method is simple and less time consuming than the conventional moisture removing method. Under typical operating conditions, the sampling rate was about 20 samples h^{-1} capable of on-line monitoring THMs in chlorinated drinking water. The detection limits of this system were found to be about 2 ppt, 4 ppt, 4 ppt, and 8 ppt for CHCl_3 , CHBrCl_2 , CHBr_2Cl , and CHBr_3 , respectively. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Most municipal water supply systems use a form of chlorine for drinking water disinfection. Chlorine can react with organic matter and leads to the formation of halogenated disinfection by-products. Among the by-products, trihalomethanes (THMs) are considered to be the major by-products associated with chlorine [1]. Current methods of analyzing THMs in water use purge and trap isolation followed

by gas chromatography (GC) or gas chromatography–mass spectrometry (GC–MS) analysis. This method provides reliable data but is time consuming and labor intensive. In addition, purge and trap is not a method with on-line and real-time monitoring capability.

Besides purge and trap methods, membrane introduction mass spectrometry (MIMS) has also been shown to be a valuable tool for analyzing THMs in chlorinated drinking water [2–11]. MIMS uses a membrane as the sampling device. The THMs diffused through the membrane continuously and flowed into the ionization source of the mass spectrometer. Therefore, MIMS is especially applicable

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to on-line monitoring. The capability of providing real-time information represents a significant advantage over the conventional purge and trap techniques. On-line MIMS can obtain total THMs concentration, as in the case of the purge and trap methods [12]. However, it is difficult to quantify chloroform and bromodichloromethane separately because both chloroform and bromodichloromethane have the same base peaks, m/z 83 and m/z 85, in the EI mass spectra.

Combining chromatography with MIMS offers the possibility of taking advantage of both chromatography as a separation method and MIMS as a real-time sampling and identification device. However, by coupling MIMS with conventional capillary GC [13], the on-line monitoring characteristic of MIMS is lost because, generally, it takes more than 10 min for a conventional capillary GC separation.

Recently, gas chromatography has used a short column for fast separations and showed great potential for reducing analysis time in many applications [14–16]. Dramatic reduction in separation time could lead to the on-line coupling of GC with MIMS without losing the on-line monitoring characteristic of MIMS. The main purpose of this study is to develop a system with the capability of GC separation and also without losing the on-line monitoring characteristic of MIMS. A system based on membrane introduction and fast GC–MS was developed. The potential and the utilities of this system were discussed in this paper.

2. Experimental

2.1. Chemicals and reagents

Aqueous stock standard solution was prepared by diluting 100 $\mu\text{g ml}^{-1}$ THMs–MeOH stock standard solution (from Chem-Service, LOT:195-116A). The standard solutions were prepared by serial dilution of the aqueous stock solution with reagent water. The toluene-d8 (from Aldrich) internal standard solution was prepared by dissolving pure standards into reagent water.

2.2. Apparatus and procedure

The instrumentation used in this study consisted of

a laboratory-built purge-type membrane introduction system, the cryofocusing unit of a Takmer 6000 AERO Trap Desorber and a Fisons GC 8000/MD 800 GC–MS. The cryofocusing unit of a Takmer 6000 AERO Trap Desorber was used as the interface between the membrane introduction system and the GC–MS. A 5-m DB-5MS (J&W Scientific, cat. no. 1225532, 0.250 mm I.D., 0.25 μm film thickness) capillary column was used for separation and 9 cm of the column was mounted inside the cryofocusing unit as the trap. The column temperature was kept at 50°C. The interface and ion source temperatures of GC–MS were set at 200°C. The MS was operated in selected ion monitoring (SIM) mode. Four ions, 83, 98, 129, and 173 were monitored. The m/z 83 ion is the base peak of chloroform and bromodichloromethane. The m/z 98, 129, and 173 ions are the base peaks of toluene-d8, dibromochloromethane, and bromoform, respectively. The scan rate was 0.112 s cycle⁻¹ giving at least 8 data points per peak.

The membrane introduction system was constructed from a 4-cm piece of stainless tube (0.085 in. I.D. \times 1/8 in. O.D.) and two Swagelok T-unions (1/8 in.). An 8-cm Dow Corning silastic hollow fiber membrane (SILASTIC[®] Medical Grade Tubing, 0.025 in. I.D. \times 0.047 in. O.D., Dow Corning, cat. no. 602-155) was mounted inside the stainless tube. The exposed length of the hollow fiber membrane in the membrane introduction system was about 5 cm. The membrane introduction system was set up so that the carrier gas flows over the outside of the membrane while the sample solution flows inside the membrane (Fig. 1). In this configuration, the ratio of surface area to the volume of the solution is larger than the sample solution flowing outside of the membrane, thereby increase the rate of analyte transport through the membrane [17]. During operation, a sample stream continuously flowed through the membrane introduction system using a peristaltic pump (Cole-Parmer MasterFlex, model no. 7524-00, with an Easy-load pump head, model no. 7518-10), typically at a flow-rate of 1.2 ml min⁻¹. The internal standard solution (toluene-d8) was pumped continuously into the flow stream by a syringe pump (Cole-Parmer E-74900-00 Infusion pump). After passing through the mixing coil (Teflon tubing 0.030 in. I.D. \times 0.062 in. O.D. \times 3 m), the internal standard solution was mixed with the sample solution and flowed into the hollow fiber tube membrane. To avoid the contami-

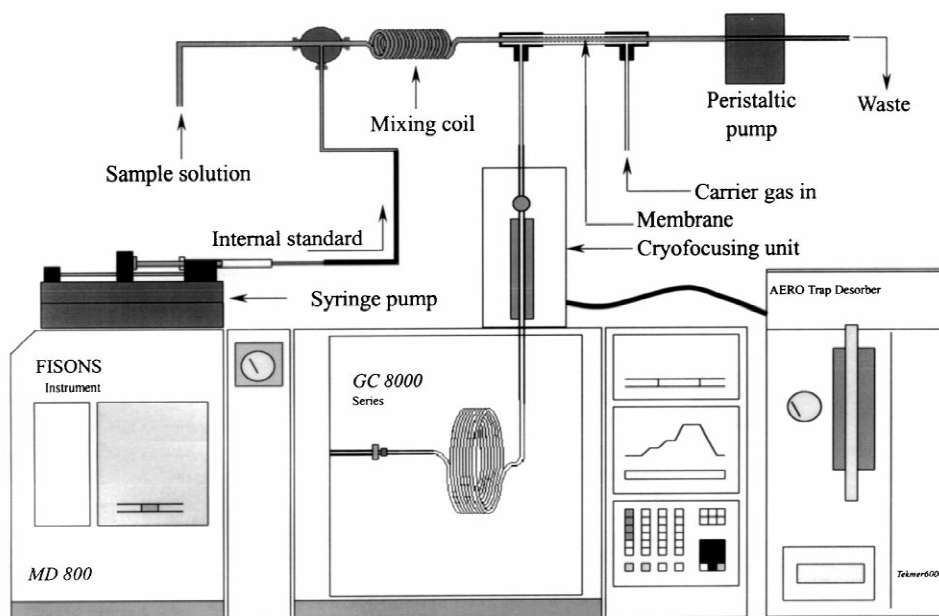


Fig. 1. Setup of the membrane introduction-fast GC-MS system.

nation of the peristaltic pump, the pump was located downstream of the flow system. A continuous flow of helium, flow-rate 1.6 ml min^{-1} , was supplied to the membrane introduction system. The flow was controlled with a regulator and the flow-rate was measured using a digital bubble flow meter at the outlet of the column. The helium flow carries the components directly into the cryofocusing system before entering the GC-MS.

The procedures of the analysis can be divided into three steps; pervaporation, preconcentration and fast GC-MS. The THMs were separated from the sample stream continuously by permeation across the membrane by the process of pervaporation. In the preconcentration and focusing step, the trap was cooled to -165°C by a continuous flow of liquid nitrogen and the THMs were collected in the trap from the sample/helium flow. It took about 1 min to cool down the trap from 200°C to -165°C . To end sample collection, the temperature of the trap was quickly increased (about $500^\circ\text{C min}^{-1}$) to the injection temperature, and then maintained at the injection temperature during the injection step (Fig. 2). The THMs in the trap were released into the separation column and detected by MS. The injection time includes the time needed to reach the injection

temperature and the time duration at the injection temperature. After the injection step, the temperature of the trap was increased to 200°C at about $500^\circ\text{C min}^{-1}$, and the system was ready for the next analysis.

3. Results and discussion

Although silicon tubing can selectively transfer THMs through the membrane, water molecules may

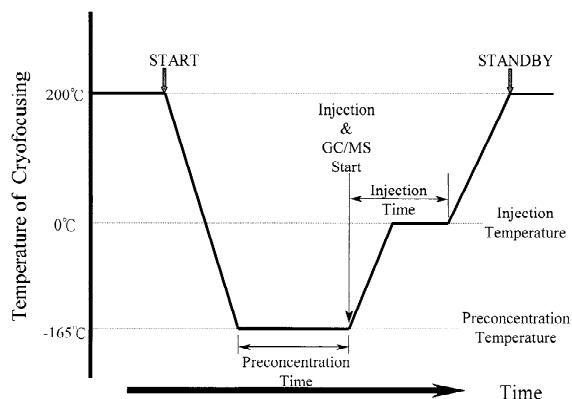


Fig. 2. The time-temperature profile of cryofocusing unit in one cycle of analysis.

also cross the membrane [7,18]. The presence of water can cause many problems [18–20] and several procedures have been proposed to avoid the effects of water [19,21–23]. Initially, to remove moisture before the GC–MS analysis, a moisture control system (MCS), the Tekmer 6000, was used. The results showed that although this system was effective in removing moisture, it normally took several minutes to remove the water. Furthermore, the recovery of bromoform was not good. To enhance the recovery of bromoform and also to reduce the cycle time as much as possible, the moisture-removing step was deleted from the analytical cycle. With this arrangement, THMs were concentrated and focused on the inlet of the separation column (trap) before the fast GC–MS analysis.

Initially, a high injection (desorption) temperature, such as 200°C, was used for injecting THMs into the analytical column. However, it was found that the sensitivity and precision for dibromochloromethane and bromoform were poorer than for chloroform and dichlorobromoform. A broad background peak re-

sulting from water was observed and this peak overlapped with the peaks of dibromochloromethane and bromoform if the concentrations of THMs were in the low ppb or ppt range. Water is believed to be responsible for these problems. The amount of water flashed into the MS is so large that not only is the baseline raised slightly (the broad background peak), but the ionization efficiencies of the dibromochloromethane and the bromoform are also suppressed by water molecules.

To overcome the problems resulting from water, a strategy based on programmed temperature vaporization injection was developed. It is hoped that by controlling the temperature of the trap and the time duration of the injection, water will remain in the trap during injection and be released into the column and ionization source after the separation and ionization of THMs. The effect of injection temperature is shown in Fig. 3. As shown in Fig. 3, the peaks of dibromochloromethane and bromoform overlapped with the background peak at injection temperatures of 10, 50 and 200°C but not at 0°C. This data

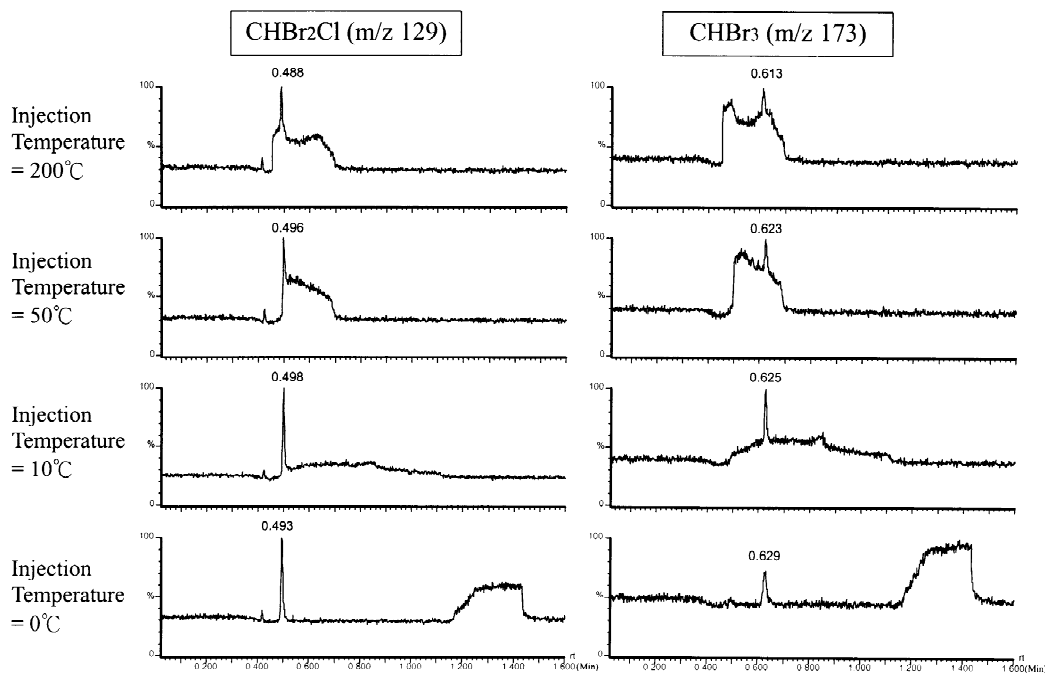


Fig. 3. The effect of injection temperature. A 25 ppt THMs standard solution was used as the sample solution without adding internal standard. The flow-rate of the sample stream was 1.2 ml min⁻¹. The preconcentration time was set at 1 min and the injection time was set at 1 min.

suggested that the moisture would not interfere with THMs if the injection temperature was controlled at 0°C during the injection step. With an injection temperature of 0°C, while THMs were injected into the column, the majority of the water molecules remained in the trap. After the injection step, water was desorbed into the column by ramping the injection temperature to 200°C (standby position). In the experiment, the injection time was set to 1 min, and it took ~0.2 min for water to go through the column. Therefore, the “water peak” was observed at ~1.2 min.

With a 0°C injection temperature, the moisture will interfere with the peak of bromoform if the injection time is less than 0.6 min. Fig. 4 showed the effect of the injection time. The chromatograms revealed that the water peak overlapped with the peak of bromoform if the injection time was 0.4 min. This is due to the fact that after the injection step, the temperature of the trap is quickly raised to 200°C (standby position) and the moisture is flushed into the separation column. The less retained water

molecule will catch up with the bromoform if the injection time is less than 0.4 min. Water took about 0.2 min to pass through the 5-m column. Therefore, if the injection time was set larger than 0.6 min, the retention time of water was longer than 0.8 min and the signal of water would not overlap with the peak of bromoform (about 0.62 min).

After the optimization, a typical chromatogram for THMs is shown in Fig. 5. The separation time was significantly less than the conventional purge and trap GC method [24]; THMs and toluene, the internal standard, could be separated in 40 s. The stability of the system was tested by on-line monitoring of a 10 ppb standard THMs solution. For 8-h on-line monitoring, the relative standard deviation for each compound ranged from 6.0% to 11.9%.

The detection limits of THMs in reagent water were evaluated. The 2, 4, 6, 8, and 10 ppt THMs standard solutions were prepared by serial dilution of THMs stock solution with reagent water. Before the test, reagent water was flowed through the membrane over 24 h to avoid contamination. The detection

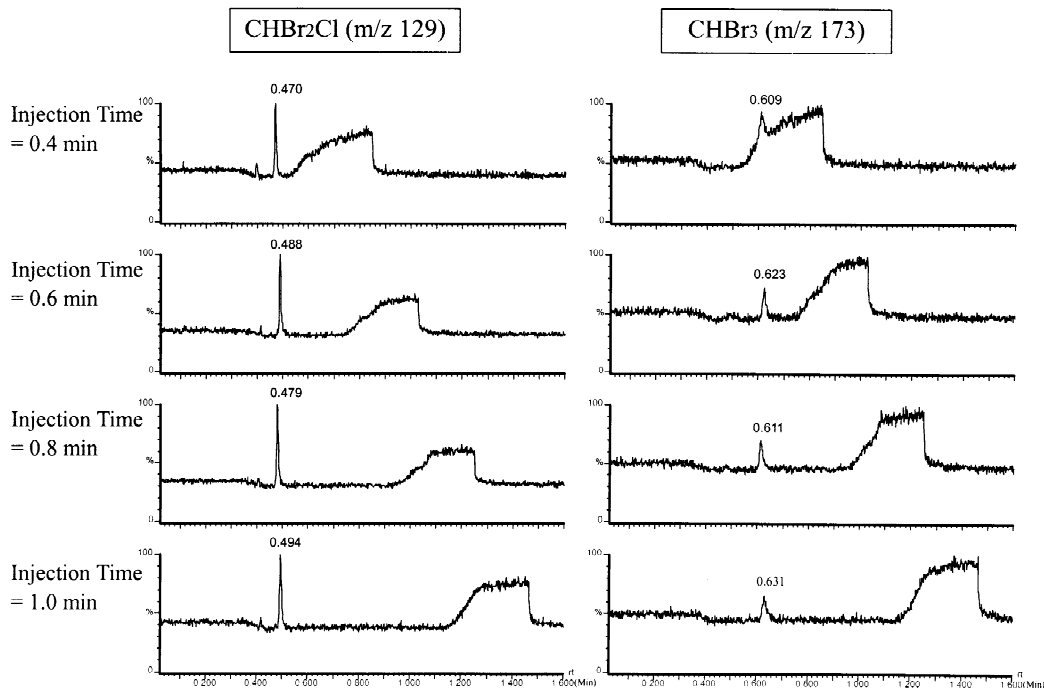


Fig. 4. The effect of the injection time. A 25 ppt THMs standard solution was used as the sample solution without adding internal standard. The flow-rate of the sample stream was 1.2 ml min⁻¹. The preconcentration time was 1 min, and the injection temperature was set at 0°C.

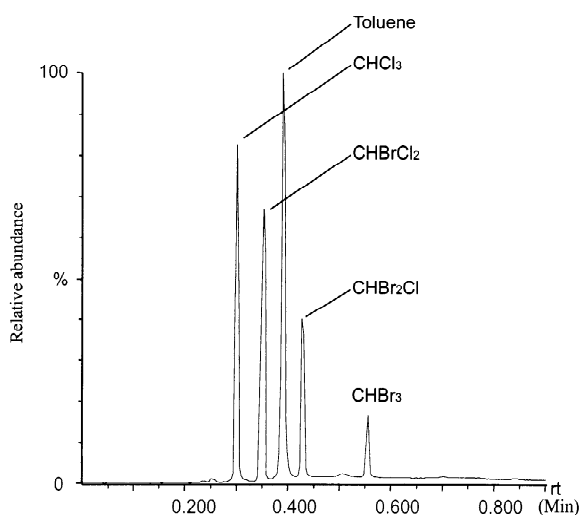


Fig. 5. Chromatogram of THMs and toluene (internal standard) obtained by membrane introduction–fast GC–MS. A 10 ppb THMs with 2 ppb toluene solution flows through the membrane introduction system continuously with 1.2 ml min^{-1} flow-rate.

limits were found to be about 2 ppt for chloroform, 4 ppt for bromodichloromethane, 4 ppt for dibromochloromethane, and 8 ppt for bromoform.

Calibration curves from 25 ppt to 20 ppb were

established based on the peak area ratio of THMs/toluene-d8. The relative standard deviation for each compound was below 9.5% (each datum was the average of three analysis for every concentration) and the correlation coefficients of THMs were better than 0.993. For a smaller and also more practical range (1–20 ppb), the relative standard deviations of the points were in the range 0.45–5.40% and the correlation coefficients were in the range 0.994–0.999. The precision and accuracy of the method were evaluated by analyzing a 4-ppb THMs standard solution. The relative standard deviations for each compound ranged from 1.4% to 4.4%, and the accuracy, expressed as the percent difference between the known and the measured concentrations, ranged from 3.0% to 8.3%.

This membrane introduction–fast GC–MS system has been tested for the on-line monitoring of THMs in Taipei municipal tap water. The chlorinated tap water was flowed directly through the membrane introduction system and analyzed by fast GC–MS. The results of a 48-min on-line monitoring test are shown in Fig. 6. These data suggest that the concentrations of THMs did not change significantly during the 48-min interval. The average concen-

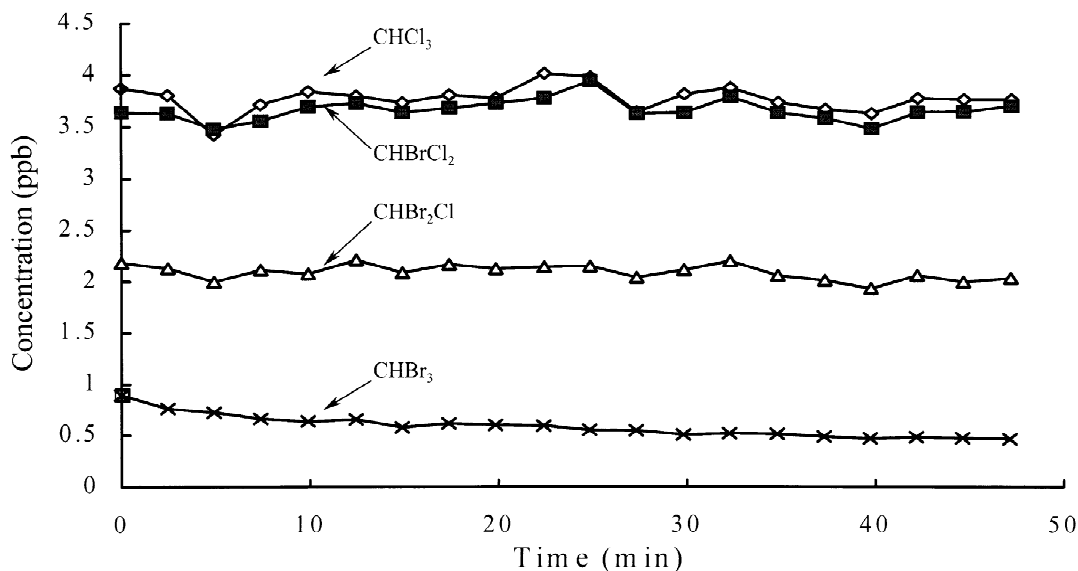


Fig. 6. Concentration vs. time profile of on-line monitoring of chlorinated tap water by membrane introduction–fast GC–MS. The flow-rate of the sample stream was 1.2 ml min^{-1} . The preconcentration time was set at 0.5 min and the injection temperature was maintained at 0°C for 0.8 min.

trations of the THMs in the tap water were 3.8 ppb for CHCl_3 , 3.7 ppb for CHBrCl_2 , 2.1 ppb for CHBr_2Cl , and 0.6 ppb for CHBr_3 .

4. Conclusions

The coupling of the membrane introduction and fast GC–MS provides a system capable of on-line and real-time monitoring of THMs in chlorinated water. While maintaining the on-line monitoring characteristic of traditional membrane introduction mass spectrometry (MIMS), the difficulty of distinguishing chloroform and bromodichloromethane in MIMS was overcome by fast GC separation. With the use of a programmed temperature vaporization injection technique, the problem of water can be overcome and the cycle time can be reduced to less than 3 min. Although water had not been prevented from entering the column, no deterioration of column performance was observed for a period of more than 1 year. This is most likely due to the fact that because of the use of silicon membrane, the amount of water trapped during sampling is much less than the conventional purge and trap. Furthermore, the oven was maintained at a relatively low temperature (50°C). This analytical system is believed to be suitable for on-line real-time monitoring of volatile organic compounds in industrial and environmental samples, especially when the specification provided by mass spectrometry as in MIMS is not adequate for identification.

Acknowledgements

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