GENERATION OF TRACE AMOUNT OF ACROLEIN STANDARD GAS USING REACTION
GAS CHROMATOGRAPHY

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A new method for the generation of acrolein standard gas has been described. It is based on the dehydration of glycerol by using potassium hydrogen sulfate as the catalyst. Comparing the results with formerly reported allyl alcohol oxidation method, the present method provides easier and much reproducible means for the preparation in the nanogram range.

INTRODUCTION

Lately, there is an increase in the request for reliable standard samples in various fields of analysis. In gas analysis, standard gases are used to obtain the calibration curves and to check the correct functioning analytical instruments and procedures.

Usually, standard gases are prepared either statically or dynamically. The static method is rather easy to prepare, but lacks in reliability on account of adsorption on the wall of the container and concentration change, especially in the low concentration range. Dynamic method, usually dilution method, is more reliable, but needs a large quantity of diluent gas and almost all gas prepared is practically wasted. Further, in the case of reactive, toxic and/or stinking gases, caution should be taken in preparing and preserving.

Recently, the use of chemical reactions in the gas chromatographic system to generate standard gases was proposed by Freed and Majsce.¹⁾ Vinyl chloride, acrolein, acrylonitrile and nitrosamines etc. were quantitatively generated through oxidation or thermal decomposition reactions. Tsang and Walker²⁾ also reported the generation of aldehydes through the stoichiometric decomposition reactions.

These results show that the chemical reaction method provides an accurate, reproducible and preferably simple means, and that it can produce just desired quantity of a standard.

In this report, a new preparation method for standard acrolein, which is based on the dehydration of glycerol, has been described. Comparison of it with the reported method revealed that our new method is superior in various points such as repeatability, life of reactor, etc.

EXPERIMENTAL

Apparatus

The system used for the generation of acrolein from glycerol by dehydration or from allyl alcohol by oxidation is presented in Fig.1. A Shimadzu Model GC-6APTH

gas chromatograph equipped with a flame ionization detector was used after modification of its carrier gas line by installation of a four way valve. Pure nitrogen gas was used as carrier gas. By choosing the position of the four way valve, nitrogen gas can be led either directly into the injection port of the gas chromatograph or by way of the reaction precolumn. Two different gas chromatographic conditions were employed for acrolein

Fig. 1 Schematic diagram

separation. For dehydration method, a glass column (2m x 3mm i.d.) packed with Chromosorb 108 (80-100 mesh) was used at 130 °C under nitrogen gas flow rate of 30 ml min⁻¹. For oxidation method, a glass column (2m x 3mm i.d.) packed with Chromosorb 105 (80-100 mesh) was used at 160 °C under nitrogen gas flow rate of 40 ml min⁻¹.

Reaction precolumn

A pyrex glass column (6mm i.d., 8mm o.d.) packed with reagent powder was used for the reaction precolumn. Outside of the tube was surrounded with a cylindrical furnace, and its temperature was controlled through a transformer.

For dehydration method, the precolumn packing was prepared through coating potassium hydrogen sulfate on Gaschrom R (60-80 mesh). Percentage of potassium hydrogen sulfate was changed (10, 20 or 30 %). The packing length was about 14 cm and each end was plugged with quartz wool. Before use, the precolumn was conditioned at 300 °C for a night.

For oxidation method, potassium dichromate (30-60 mesh) was used as the precolumn packing. Its packing length was about 8 cm, and each end was plugged with quartz wool. Preconditioning was also done at 300 °C for 24 h.

Materials

Glycerol and allyl alcohol were both reagent grade and obtained from Tokyo Chemical Industry (Tokyo). Potassium dichromate and potassium hydrogen sulfate, both reagent grade, were from Kanto Chemical Industry (Tokyo). Acrolein obtained from Tokyo Chemical Industry was used after purification by distillation.

RESULTS AND DISCUSSION

Oxidation method

Aqueous solutions of allyl alcohol in various concentrations ($1.7 \times 10^{-3} \text{ g l}^{-1}$ — $1.7 \times 10^{-1} \text{ g l}^{-1}$) were prepared and acrolein was generated by injecting a few microliters of the solution directly into the precolumn.

Effects of precolumn temperature and nitrogen gas flow rate on the reaction were similar to reported by Freed and Majsce.¹⁾ The optimum reaction temperature was 260 °C, and that of carrier gas flow rate was 40 ml min⁻¹. Under the optimum conditions, a linear relationship between injected amount of allyl alcohol and generated amount of

acrolein in the range of 3 to 600 ng was obtained. The reaction yield was 94.5 %. As for repeatability, the relative standard deviation was 3.6 % with 20 injections of 170 ng of allyl alcohol.

This method has, however, at least two shortcomings. First, the range of optimum reaction temperature was limited to about 260 °C. (Fig.2) When the temperature was lower than 250 °C, there appeared unreacted allyl alcohol because of incompleteness of the reaction.

On the contrary, when the temperature was higher than 270 °C, oxidation proceeded further to give acrylic acid or polymers. Therefore, careful temperature setting was necessary. Second, repeatability was poor. The relative standard deviation was 3.6 %. It was considered that the reaction could not be carried out under steady conditions, since decrease of oxidation ability or formation of channels in the precolumn packing resulted. Further, surface of the reagent was changed gradually to chromium oxide by reduction.

Silver oxide also was attempted instead of potassium dichromate as the precolumn reagent, but it was not suitable for the generation of acrolein because adsorption and side-reaction seemed to occur.

Dehydration method

In order to ameliorate the shortcomings of the oxidation method, a new reaction, dehydration of glycerol, was investigated. In this case, aqueous glycerol solutions ($1.5 \times 10^{-3} \text{ g l}^{-1}$ — $1.5 \times 10^{-1} \text{ g l}^{-1}$) were prepared and a few microliters of the solution was injected into the reaction precolumn. Acrolein generated was confirmed by gas chromatography-mass spectrometry.

Dehydrating reagent

First of all, potassium hydrogen sulfate and sodium hydrogen sulfate were examined for the dehydrating reagent. In both cases, generated amount of acrolein was maximum at about their melting points. But the yield with sodium hydrogen sulfate was much poorer than with potassium hydrogen sulfate. Therefore, the latter was chosen for the dehydration reagent.

Potassium hydrogen sulfate was packed into the precolumn after coated on Gaschrom R (60-80 mesh). Coating percentages of 10%, 20% and 30% were examined. When the coating amount was 10% or 20%, the generated amount of acrolein was similar and satisfactory. In case of 30%, however, the amount generated decreased gradually and

Fig.2 Yields vs. temperature
Flow rate is 40 ml/min
(○) Acrolein
(Δ) Allyl alcohol

the precolumn was finally clogged. Consequently, 10% was chosen for coating amount of potassium hydrogen sulfate.

Reaction time

It was found that dehydration of glycerol catalysed with potassium hydrogen sulfate needed a certain time for completion of the reaction. Therefore the time required for completion of the reaction was investigated. Reaction time was controlled by switching the four way valve shown in Fig.1. Under three different reaction temperatures i.e. 240, 250 and 260 °C, the relation between reaction time and generated amount was obtained as shown in Fig.3. The amount of glycerol injected was 150 ng. As shown in Fig.3, maximum yields can be obtained when the reaction time is between 1 and 2.5 min. When the reaction time was less than 1 min, generated amounts were scarce because of incompleteness of the reaction. Generated amounts also became small when the reaction time was more than 3 min. Thermal decomposition of acrolein was supposed to occur. An appropriate reaction time was found to be 1.5 min. No effect of injection volume was observed.

Reaction temperature

Optimization of reaction temperature was also performed under injection amount of glycerol 150 ng and reaction time of 1.5 min. The result is shown in Fig.4. When the temperature was higher than 260 °C, generated amount was maximum and constant even if the injection volume was changed. Therefore 280 °C was chosen as the optimum temperature.

Fig.3 Yields vs. reaction time

Fig.4 Yields vs. temperature

Linearity of calibration plot

Under the optimum conditions, relation between injected amount of glycerol and the amount of acrolein generated was examined. A linear relation was found in the range of 5 to 300 ng. The reaction yield was 96.3 %. As for the repeatability, the relative standard deviation was 0.82 % with 20 injections of 120 ng of glycerol.

Comparison of the two method

In Table 1, the oxidation method and dehydration method were compared. The reaction temperature of the oxidation method must be approximately around 260 °C. In the proposed method, however, any temperature over 260 °C can be used and generation of acrolein is stable even if the temperature varies in some measure.

Next, in the oxidation method, the precolumn reagent is consumed because of the change of potassium dichromate to chromium oxide by reduction. Contrary, in the proposed method, the consumption of the reagent is very little and durability is good enough because potassium hydrogen sulfate acts only as the catalyst.

The lower limits of generatable amounts are almost the same. These values are determined mainly by the lower limit of detection of the detector employed.

Finally, the repeatability in the oxidation method is poorer than the proposed method.

Table 1 Comparison of the oxidation method and the dehydration method

	Oxidation of allyl alcohol	Dehydration of glycerol
Temperature range	260 °C	over 260 °C
Reagent consumption	much	less
Lower limit of generation	5.2×10^{-11} mol	5.4×10^{-11} mol
Yield	94.5 %	96.3 %
Repeatability (cv)	3.6 % *	0.82 % **
Sample amount	* ; 170 ng	** ; 150 ng

In conclusion, it is advisable to use the dehydration method proposed here for the preparation of nanogram level acrolein standard gas. It provides easier and much reproducible means for the preparation.

REFERENCES

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Keyword phrases

generation of trace amount of acrolein standard gas; reaction gas chromatography; dehydration of glycerol; reaction precolumn.

(Received June 4, 1983)