

## Microdetermination of Molecular Weight\*

The previous study conducted in 1957 (1) indicated that the isothermal distillation method was better than the ebullioscopic and cryoscopic methods. Only 10 collaborators participated in the initial study and only three used the isothermal distillation procedure. This year an appeal was made for other collaborators using the method to provide data on the same test samples analyzed last year. Three sets of data were received, one from a collaborator who participated last year, and two from analysts who used a new approach to the problem.

This new method is an isothermal process only in that distillation takes place in a constant temperature atmosphere but, instead of establishing equilibrium between two solutions, the temperature difference

between a solvent and solution in a saturated atmosphere of the solvent is measured. This temperature difference is caused by the differences in rate of evaporation and condensation for the solution and solvent; the two rates are equal for the solvent but different for the solution with the rate of condensation exceeding that of evaporation. Thus a rise in the temperature of the solution, as compared with the solvent, is caused. The temperature difference is measured by thermistors.

Müller and Stolten (2) and Neumayer (3) have described apparatus and procedures for this determination. A third apparatus has been developed and was described at a recent scientific meeting. The method of Neumayer requires only 3-5 mg of sample and only 3 minutes to reach temperature equilibrium.

The complete determination, including preparation of the solution, adjusting the

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apparatus and making the determination, should not require more than 30 minutes. The short time required for an analysis is the great advantage of this procedure over the conventional isothermal distillation method which requires several days' elapsed time before a result can be obtained. The disadvantage is that the apparatus for the thermistor method (Wheatstone bridge, thermistors, sensitive null indicator, battery and cell), if not already available, would cost about \$300.

As mentioned above, the main criticism of the isothermal distillation method is the time required to obtain equilibrium between the two solutions. This Referee has been attempting to design an apparatus which would materially shorten the time required and has been only partially successful. Another apparatus employing a different approach to the problem is being tested in this laboratory. If the apparatus proves satisfactory, it should be possible to test the apparatus and method during the coming year. For the conventional method to compete with the thermistor method the time required for equilibrium would have to be reduced to 16-24 hours.

### Results and Recommendations

The results obtained by the three collaborators are shown in Table 1. Those by the thermistor methods (Collaborators 51 and 75) show that good values for molecular

weight, using micro samples, can be obtained in minutes rather than days as required by the isothermal distillation procedure. The accuracy and precision obtained by Collaborator 75 with the new thermistor method are both excellent. If the time required for the isothermal distillation method cannot be very much reduced, the thermistor method will probably be the one most used in the future. Although both of these methods show promise of being acceptable as official methods, there are too few collaborators using either method at present to permit reliable collaborative tests.

It is recommended<sup>1</sup> that the study be continued to try to improve on the isothermal distillation method and obtain more collaborators.

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### REFERENCES

- (1) Ogg, C. L., *This Journal*, **41**, 294 (1958).
- (2) Müller, R. H., and Stolten, H. J., *Anal. Chem.*, **25**, 1103 (1953).
- (3) Neumayer, J. J., *Anal. Chim. Acta.*, **20**, 519 (1959).

<sup>1</sup> This recommendation was approved by Subcommittee C and was adopted by the Association. See *This Journal*, **43**, 133 (1960).

Table 1. Results of molecular weight determinations

Method	Thermistor	Isothermal	Thermistor <sup>c</sup>
Benzoic Acid (122.1)			
<i>n</i>	—	1	4
$\bar{x}$	124.3 <sup>a</sup>	123	122.25
<i>s</i>	—	—	0.50
Gantrisin <sup>b</sup> (267.3)			
<i>n</i>	3	1	4
$\bar{x}$	273	260	267.8
<i>s</i>	10.6	—	1.90
Solvent	Benzene Et acetate	Methanol	2-Butanone
Sample wt (mg)	10-20	3	3-5
Vol. solvent (ml)	3-6	1	0.3
Bath temp. (°C)	30	40	30
Equilibrium time	10 min.	13 days	3 min.

<sup>a</sup> Value was obtained by extrapolation to infinite dilution because benzoic acid associated in the benzene solvent.

<sup>b</sup> 3,4-dimethyl-5-sulfanilamido-isoxazole.

<sup>c</sup> Reference (3).