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MODIFICATION OF THE CARIUS COMBUSTION TUBE TO MINIMIZE LOSSES BY EXPLOSION: PRESSURES ATTAINED ON HEATING NITRIC ACID TO 300° C

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ABSTRACT

This paper describes a modified form of tube which minimizes the likelihood of loss by explosion in the Carius method of determining halogens and sulfur in organic substances. The familiar Carius tube of Pyrex glass cannot be sealed properly in the laboratory. Residual strains in the glass seals cause the tubes to burst at pressures much lower than those to be expected from the normal strength of the glass. By sealing smaller neck-tubes on the usual heavy-walled tubes, all the seals except the small final seal can be oven-annealed at the factory.

While the bursting pressure of the unmodified tubes was found to be between 1,000 and 1,400 pounds per square inch, the modified tubes burst at over 2,500 pounds per square inch. The pressures developed during a Carius determination were estimated from determinations of the pressures developed by various amounts of fuming nitric acid in a specially designed gage. Such pressures were found to be below 1,520 pounds per square inch at temperatures up to 300° C when the amount of acid was limited to that customarily used.

A difficulty which limits the usefulness of the Carius method for the determination of halogens and sulfur in organic substances is the frequent breakage of the tubes during the decomposition with fuming nitric acid. This is so well known that the procedure has been referred to as the "precarious method." In connection with the use of sealed tubes for the decomposition of some minerals and refractory metallic substances with hydrochloric acid [7],[1] observations were made which appeared to explain the frequent failures of Carius tubes and which suggested a simple modification that will obviate most such failures.

Carius tubes as supplied in Pyrex laboratory glass are long, heavy-walled tubes, ranging up to 19 mm in inside diameter, and with a constriction near the open end to facilitate sealing. The bursting pressure of several of these tubes of 15-mm inside diameter (wall thickness approximately 2.5 mm), when sealed with reasonable care but without special attention to annealing, ranged from 1,000 to 1,400 pounds per square inch. An effort was made to "smoke" some of these seals, but difficulties in handling the filled tubes precluded any good smoking operation. The bursting pressure of tubes sealed without smoking have not differed noticeably from those "smoked."

[1] Numbers in brackets indicate the literature references at the end of this paper.

Measurements of bursting pressure were made by heating the tubes, half-filled with water, in a loosely capped piece of pipe supported in a combustion furnace [2] until steam suddenly escaping through the loosely fitted cap indicated bursting of the tube. Temperatures were measured by means of a thermocouple hard-soldered to the pipe. The corresponding pressures were taken from a table of saturated water vapor pressures [5] if below the critical temperature, or from a table of the pressure of dilated water vapor [2] if above the critical temperature. Although the bursting pressures are thus measured at different temperatures, they were considered to be comparable, since the strength of Pyrex glass is nearly constant below 400° C.

The bursting pressure of well-annealed glass tubes of the dimensions given, and made with well-rounded ends, is over 3,000 pounds per square inch, calculated on the basis of a tensile strength of about 10,000 pounds per square inch [4]. It is well known that the actual strength of glass is affected by the presence of scratches or other imperfections and by strains. With the tubes in question, careful attention was given to keep the surface free from scratches, but it became evident that the ends of the tubes, sealed with the contents of the tube in place, could not be adequately annealed. A modified form of tube was then made by attaching to the open end a tube of 4-mm inside diameter and 2-mm wall thickness (4 by 8 mm). The tube thus made was oven-annealed before use. The tube was charged through this neck of smaller bore and sealed without any attempt at annealing.

Tubes made in this way did not burst at pressures of water vapor less than 3,100 pounds per square inch. Sections of the 4- by 8-mm tubing alone, with both ends sealed without special precautions, burst at pressures greater than 5,000 pounds per square inch. This is about one-half the theoretical bursting pressure calculated on the basis of a tensile strength of 10,000 pounds per square inch. Several pieces of standard-wall tubing 7- by 9.5-mm burst at about 2,100 pounds per square inch, which is 50 to 100 percent above the pressure at which the unmodified Carius tubes burst. If Carius tubes are made with attached necks of 6-mm inside diameter and 9- to 10-mm outside diameter, failures by bursting should be very infrequent. Such tubes are also easier to seal and easier to open for removal of the contents than those now available. An inside diameter of the neck of 6-mm is sufficient to allow easy introduction of the sample in a glass capsule.

In order to estimate the pressure that may occur in Carius tubes, measurements were made of the pressures developed by fuming nitric acid in sealed tubes at temperatures up to 300°C. These measurements were made by enclosing the acid in a glass U-tube with the bend flattened like a Bourdon tube. A change in pressure within the tube caused movement of the arms, which was balanced by a compensating gas pressure within a steel bomb and observed by the opening or closing of an electrical circuit through a pair of platinum-iridium contacts attached to the ends of the arms. The compensating pressures were read on a Bourdon gage to within 5 pounds per square inch.

Since nitric acid is not a single-component system, the pressures generated by different amounts of the acid in a given total volume are different. Two sets of measurements of the pressures generated by

[2] Carius decompositions can be conducted in a similar manner, if the customarily used bomb furnace is not available. The pipe can be made the furnace itself by covering it with a layer of asbestos paper over which is wound a spiral of resistance wire and several more layers of asbestos paper.

fuming nitric acid (sp gr at 25° C of 1.48) are shown in figure 1. The two curves are for different "mean densities", which are the total grams of nitric acid solution per 100 ml of total volume. Curve A shows the pressures attained by 63.2 g of acid per 100 ml (or 42.7 ml/100 ml at 25° C). This quantity is nearly that mistakenly recommended for use in the Carius procedure by some textbooks [1]. Curve B shows the pressures developed when the amount of acid is equal to the maximum of 8 g/100 ml suggested by Fresenius [3]. These pressures may be taken as indicative of the maximum pressure developed in a Carius determination on the assumption that the addition of the silver nitrate and the organic material affect the total pressure but slightly. From figure 1 it can be seen that in the temperature range 200° to 300° C the pressures developed are in the bursting range of the unmodified tubes previously mentioned.

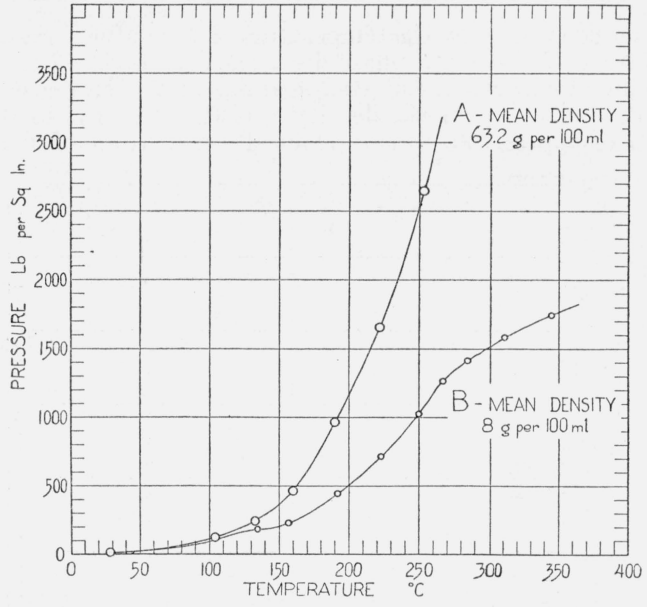

FIGURE 1.—*Pressures developed by fuming nitric acid (sp gr 1.48 at 25° C) at constant volume on heating.*

The mean density is the total amount of acid as vapor and as liquid in the tube per unit volume (100 ml).

The results from which the curves in figure 1 were constructed, together with those for one additional quantity of nitric acid, are given in table 1. Although they are not of high precision, they may be useful, especially in connection with the design of apparatus, in view of the absence of other recorded data on the pressures developed by nitric acid at elevated temperatues.

To show whether there is liquid present in the tube as used in a Carius determination when the amount of fuming nitric acid is 8 g/100 ml or less, small tubes containing various quantities of the fuming nitric acid were prepared. These were heated in a vertical glass cylinder on which was wound a resistance wire as the heating element. A thermocouple suspended in the cylinder beside the sealed

TABLE 1.—*Pressures developed at constant volume by various amounts of fuming nitric acid (sp gr 1.48 at 25° C)*

Amount of acid					
63.2 g/100 ml		18.9 g/100 ml		8.0 g/100 ml	
Temperature	Pressure (abs.)	Temperature	Pressure (abs.)	Temperature	Pressure (abs.)
° *C*	*lb/in.*²	° *C*	*lb/in.*²	° *C*	*lb/in.*²
133	245	133	180	157	230
160	465	165	380	192	445
190	965	192	630	223	715
222	1,655	219	995	250	1,025
253	2,645	256	1,565	267	1,265
		285	2,245	285	1,415
		313	2,945	311	1,585
		326	3,135	345	1,745

tube was used to measure the temperature at which (without agitation) the last trace of the liquid phase disappeared. Figure 2 shows these "dew-point" temperatures plotted against the "mean density." The tube with the highest mean density was the only one in which the meniscus disappeared before it reached the bottom of the tube.

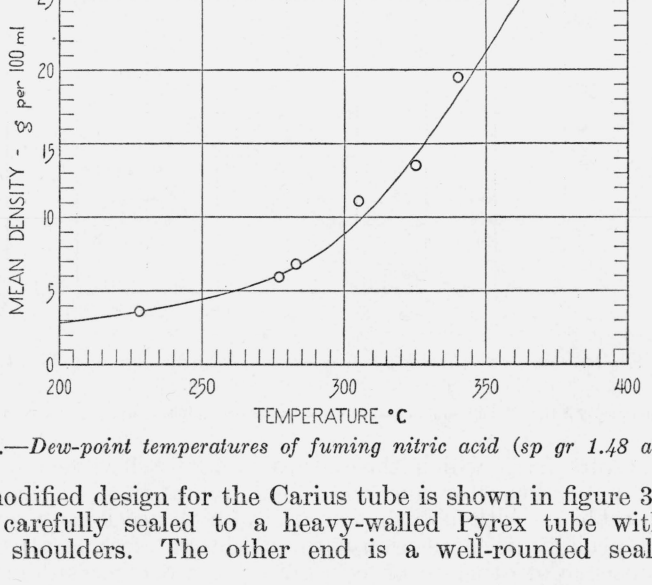

FIGURE 2.—*Dew-point temperatures of fuming nitric acid (sp gr 1.48 at 25°C).*

The modified design for the Carius tube is shown in figure 3. The stem is carefully sealed to a heavy-walled Pyrex tube with well-rounded shoulders. The other end is a well-rounded seal. The

FIGURE 3.—*Modified Carius tube.*

The volume of the main tube is approximately 0.57 ml/cm, the tube is made of such length as will permit the desired amount of nitric acid to have a mean density of 8 g/100 ml or less. The length of the neck, if 15 cm, is sufficient to permit repeated use of the tube.

whole tube is flamed to eliminate any minute surface scratches. It is then carefully annealed by heating to 560° to 580° C and maintaining within this temperature interval for at least 1 hour, followed by slow cooling [6]. The tubes thus made should be kept individually wrapped, to prevent scratching of the finished surface while they are stored before use.

For the final sealing of the tube, a simple and satisfactory technic is as follows: Clamp the tube in a vertical position. Warm the neck slightly below the open end to cause an expulsion of air. Heat the open end until it flows together. A very hot flame (oxygen-gas) is necessary for this so that the end will fuse completely without leaving a pinhole. The fused end may suck back slightly but can be blown out round by rewarming the neck below the seal and applying the hot flame across the top of the seal to heat the thickened portion, but not the sides. Skill in making such seals can be acquired with a little practice on pieces of tubing identical with that used for the necks, which have been previously closed at one end.

When decomposition of the organic substance is completed, excess pressure in the tube is released as usual by heating the tip of the seal and allowing it to blow out. A short section of the neck can then be cut off, leaving the main part of the tube intact. The tubes can then be rinsed through the neck by any convenient means. Any silver chloride adhering to the interior of the tube can be removed with ammonium hydroxide. If only a short piece of the neck is cut off to open the tube, the tube can be used for several determinations, inasmuch as nitric acid under pressure and elevated temperature (as contrasted with hydrochloric and hydriodic acids), does not attack the glass to such an extent as to make resealing unfeasable. A tube saved in this manner and used three times was subsequently found to burst at over 4,000 pounds per square inch.

Carius micro determinations can be made in 4- by 8-mm heavy-walled Pyrex tubes sealed without annealing. Such tubes withstand pressures above 5,000 pounds per square inch. The volume can be adjusted as required by using a tube of the necessary length. The capacity of this tubing is approximately 0.125 ml per cm of length. A small capsule of 2- by 3-mm tubing may be used for the sample. In these tubes a larger amount of nitric acid per unit volume is permissible because of the greater strength of the tube.

[1] W. W. Beshgetoor, Ind. Eng. Chem., Anal. Ed. **1,** 92 (1929).
[2] N. E. Dorsey, The Properties of Ordinary Water-substance, table 36, page 87 (Reinhold Publishing Corporation, New York, N. Y., 1940).
[3] C. R. Fresenius, Quantitative Chemical Analysis, vol. II, p. 118, translation of 6th German edition by A. I. Cohn (John Wiley & Sons, New York, N. Y., 1904).
[4] G. W. Morey, The Properties of Glass, p. 330, (Reinhold Publishing Corporation, New York, N. Y., 1938).
[5] N. S. Osborne and C. H. Meyers, J. Research NBS **13,** 1 (1934) RP691.
[6] Pyrex Brand Laboratory Glassware, catalog LP 21, p. 7, Corning Glass Works, Corning, N. Y. (1941).
[7] E. Wichers, W. G. Schlecht, and C. L. Gordon (unpublished work).

WASHINGTON, November 27, 1942.