

buffer flow rate F can then be increased without exceeding the desired carry-over of B .

Nonmixing greatly increases the over-all efficiency of the continuous-flow operation; it is nevertheless much slower and much less efficient than batch fractionation. For example, separating BGG and BSA by a three-stage batch electroconvection gave 94-percent recovery of 100-percent pure BGG in 200 ml of solution and 100-percent recovery of 97-percent pure BSA in 40 ml of solution; total time, 72 hr, as compared with 155 hr for the continuous-flow operation.

A more complete treatment, including an extension of the foregoing theory to other systems, is given elsewhere (9).

References

1. A. Polson, *Biochim. et Biophys. Acta* **11**, 315 (1953).
2. S. N. Timasheff, J. B. Shumaker, and J. G. Kirkwood, *Arch. Biochem. and Biophys.* **47**, 455 (1953).
3. P. Stamberger, Brit. Pat. 505753 (1936).
4. ———, Brit. Pat. 505752 (1936).
5. W. Pauli, *Helv. Chim. Acta*, **25**, 137 (1942).
6. P. Stamberger, *J. Colloid Sci.* **1**, 93 (1945).
7. R. A. Brown *et al.*, *J. Am. Chem. Soc.* **73**, 4420 (1951).
8. J. G. Kirkwood, J. R. Cann, and R. A. Brown, *Biochim. et Biophys. Acta* **6**, 606 (1950).
9. S. Raymond, *Electroconvection* (E-C Apparatus Co., New York, 1954), 72 pp.

10 May 1954.

Retention of Chromium by Glass Following Treatment with Cleaning Solution

E. B. Butler

Libbey-Owens-Ford Glass Company, Toledo, Ohio

W. H. Johnston

Department of Chemistry, Purdue University, Lafayette, Indiana

Over a period of years we have heard the remark that traces of chromium are retained on glassware that has been treated with the common laboratory cleaning solution of alkali metal dichromate and sulfuric acid. These comments frequently included cautions against possible interferences of the retained dichromate ions in precision measurements of surface tension and in some biological enzyme reactions. A literature search has revealed only one direct assay of the magnitude of this effect. In 1934, Laug made a colorimetric estimation of the retention of dichromate ion on several pieces of Pyrex brand and of lime glasses (1). He reported a few micrograms as $K_2Cr_2O_7$ in the wash waters following treatment by cleaning solution for 6 to 30 days. In view of the semiquantitative nature of this study and a limit of sensitivity of about 0.2 μg $K_2Cr_2O_7$, it was thought desirable to reconsider this problem in the light of modern radiochemical techniques.

Low-level counting techniques (2) and in particular the use of a stable sodium iodide scintillation spectrometer (3) for counting a gamma emitter such as Cr^{51} make possible detection sensitivities of orders of magnitude greater than the conventional colorimetric methods. High specific activity chromium chloride

from the Atomic Energy Commission was converted to dichromate cleaning solution and used for a study of the retention of chromium on quartz, Pyrex brand, and commercial plate glass. The limit of detection by direct measurement of the glass surfaces was 10^{-4} μg as $K_2Cr_2O_7$, despite the fact that only 8 to 10 percent of the disintegrations of Cr^{51} are accompanied by gamma emission. The observed retentions exceeded this limit. It was, therefore, possible to count these samples by both the scintillation spectrometer and a Geiger counter.

The Cr^{51} was precipitated as the hydroxide and freed from chloride ion. The chromic ion was converted to dichromate by oxidation with excess hydrogen peroxide in basic solution. The excess peroxide was destroyed, and water and sulfuric acid were adjusted to approximate the usual cleaning solution (4). Some fused quartz disks 1½ in. in diameter and ¼ in. thick were on hand. Disks of the same dimensions were cut from Pyrex brand and commercial soda-lime plate glass.

In the initial experiment an area of approximately 7 cm² on one side only of these glasses was soaked at room temperature for 24 hr in radioactive cleaning solution. Each piece of glass was rinsed for about a minute in running water, dried, and counted. Tests showed that continued washing or strenuous rubbing with Kleenex did not alter the retention. The observed net counts per minute by the scintillation spectrometer (5) and by the Geiger counter are shown in Table 1. Although considerable variation is shown in Table 1, significantly more Cr^{51} was retained by the Pyrex brand glass.

Table 1. Retentions of Cr^{51} on glasses following treatment with cleaning solution (net counts per minute by Geiger counter and by scintillation spectrometer).

Instrument	Set	Fused quartz	Pyrex	Plate
Geiger counter	I	5	9	3
	II	5	12	7
Scint. spect. (Photo-peak)	I	60	229	33
	II	106	178	93

Two additional experiments were made to obtain information on the form of this retention. Samples of all three glasses were treated with a solution of chromium chloride in sulfuric acid containing the same specific activity of chromium as used in the dichromate cleaning solution. Also a sample of Pyrex brand glass was coated with grease from the face and hands and treated with the radioactive dichromate solution. These retentions are shown in Table 2.

The similarity between the data of Table 1 and set III of Table 2 suggests that the primary retention is adsorption of chromic ion rather than dichromate ion. Furthermore, the high retention on the greasy sample suggests either that adsorption of both ions occurs

Table 2. Retentions of Cr^{+3} from Cr^{+3} solution and on greasy glass from cleaning solution.

Instrument	Set	Treatment	Fused quartz	Pyrex	Plate
Geiger counter	III	Cr^{+3}	4	5	5
	IV	Grease and $\text{Cr}_2\text{O}_7^{-2}$		124	
Scint. spect. (Photo-peak)	III	Cr^{+3}	84	85	126
	IV	Grease and $\text{Cr}_2\text{O}_7^{-2}$		3590	

much more readily on the surface of the grease or that partial oxidation of the grease film by $\text{Cr}_2\text{O}_7^{-2}$ causes the Cr^{+3} produced in the oxidation to be strongly affixed to the remaining film.

According to a standard assay that checked the specific activity reported by the Oak Ridge National Laboratory for the original solution, each count per minute by the scintillation spectrometer corresponds to 3×10^{-12} mole of chromium atoms. If a figure of 200 counts/min for Pyrex is taken from Table 1, the coverage is 2×10^{-10} mole/cm² of chromium atoms. If the area per atom is assumed to be 10^{-15} cm² and if the actual area is taken as twice the geometric area, the coverage is estimated as 3 percent of a monolayer.

It appears that a negligible amount, 0.03 monolayer or less, of chromium is retained by fused silica, Pyrex, or soda-lime glass following treatment by ordinary dichromate cleaning solution. On the other hand, if the cleaning is incomplete and the grease layer is not completely removed, as much as 0.5 monolayer of chromium may be retained.

References and Notes

1. E. P. Laug, *Ind. Eng. Chem., Anal. Ed.* **6**, 111 (1934).
2. W. F. Libby, *Radiocarbon Dating* (University of Chicago Press, Chicago, 1952).
3. J. R. Arnold, *Phys. Rev.* **93**, 743 (1954).
4. *Handbook of Chemistry and Physics* (Chemical Rubber Publ. Co., Cleveland, ed. 33, 1951), p. 2722.
5. Since our low-level scintillation spectrometer was under construction at the time this work was done, we are indebted to James R. Arnold of the Institute for Nuclear Studies, University of Chicago, who kindly let us use his scintillation spectrometer.

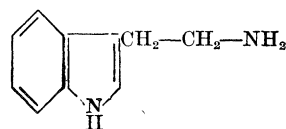
10 May 1954.

Action of Dimethylkynurenamine on Blood Pressure

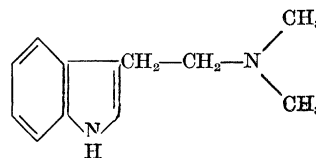
Katashi Makino and Hitoshi Takahashi

Department of Biological Chemistry,
Kumamoto University Medical School, Kumamoto, Japan

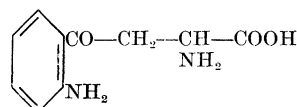
Bufotenine isolated from toad venom and serotonin from beef serum or mammalian gastrointestinal mucosa have remarkable pressor activity and vasoconstricting effect when injected intravenously into animals. Tryptamine (I) and dimethyltryptamine (II) also seem to have such an action, although it is weaker than serotonin itself.



(I)



(II)



(III)

Recently dimethylkynurenamine (III) hydrochloride (mp 158° to 160°C, yellow needle or globe; monoplicate, mp 165°C, $\text{C}_{17}\text{H}_{19}\text{O}_8\text{N}_5$: calculated C, 48.45, H, 4.51, N, 16.63; found C, 48.65, H, 4.50, N, 16.05 percent), which was presumed to be derived from dimethyltryptamine or kynurenine, was prepared, in the presence of palladium charcoal, by hydrogenation of dimethyl o-nitrobenzoyl ethylamine hydrochloride (mp 165° to 167°C; picrate, mp 143°C, $\text{C}_{17}\text{H}_{17}\text{O}_{10}\text{N}_5$: calculated C, 45.23, H, 3.76, N, 15.52; found C, 45.62, H, 3.42, N, 15.32 percent).

This dimethylkynurenamine hydrochloride had a faint jasmine-like odor and was easily soluble in water, giving a yellow color. On paperchromatogram it was recognized as a blue fluorescent spot and showed with Dragendorff reagent a reddish-orange color, with p-dimethylaminobenzaldehyde in hydrochloric acid an orange color, and with diazotized sulfanilic acid a yellow color. Its Rf value developed with the supernatant of the mixture of acetic acid, butanol, and water in ratio 1 : 4 : 5 was 0.66, with 70 percent isopropanol 0.62. Its ultraviolet absorption spectrum has: $\lambda_{\text{max}1}$, 256 m μ ; $\lambda_{\text{max}2}$, 358 m μ ; $\lambda_{\text{min}1}$, 246 m μ ; $\lambda_{\text{min}2}$, 280 m μ (pH 4.8).

Pharmacological study revealed that dimethylkynurenamine has a strong blood pressure-lowering activity in contrast to the pressor activity of tryptamine. When 100 μg of dimethylkynurenamine hydrochloride (per kilogram) was injected intravenously into the urethane-anesthetized rabbits (five rabbits, 1.5 to 2 kg), a lowering of blood pressure of 15 mm-Hg was recorded manometrically in the common carotid artery.

More remarkable action was seen with larger doses, as is indicated in Table 1.