

**128.** *A Convenient Method for the Preparation of [<sup>36</sup>Cl]Chlorine from [<sup>36</sup>Cl]Hydrochloric Acid: Decomposition of Palladous [<sup>36</sup>Cl]Chloride.*

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Quantitative yields of chlorine may be obtained by thermal decomposition of palladous chloride *in vacuo*. [<sup>36</sup>Cl]Chlorine is conveniently obtained in a vacuum system if the palladous chloride is labelled by exchange with [<sup>36</sup>Cl]hydrochloric acid before decomposition. The specific activity of the chlorine obtained is shown to be the same as that expected from the initial proportions of palladous chloride and [<sup>36</sup>Cl]hydrochloric acid selected.

THE familiar laboratory methods for the preparation of chlorine have serious disadvantages when very small amounts of the pure gas, labelled with chlorine-36, are required for introduction into a vacuum-system. Most procedures involve oxidation of hydrochloric acid, a proportion of the original chlorine being converted into a metal chloride, and the chlorine obtained usually contains some hydrogen chloride and water as impurities. Brown, Gillies, and Stevens<sup>1</sup> prepared [<sup>36</sup>Cl]chlorine by heating potassium peroxosulphate

<sup>1</sup> Brown, Gillies, and Stevens, *Canad. J. Chem.*, 1953, **31**, 768.

with dilute aqueous [ $^{36}\text{Cl}$ ]hydrochloric acid, the chlorine being swept from the solution in a stream of argon or helium. While this method overcomes some of the difficulties, the chlorine obtained may contain oxygen as an impurity, and its quantitative introduction into a vacuum-system would involve some problems.

It has been reported<sup>2</sup> that palladous chloride decomposes into palladium and chlorine at  $\sim 600^\circ$ . Experiments carried out to test whether the decomposition occurs quantitatively show (Table 1) that when the chlorine is efficiently removed by condensation at liquid-air temperature the decomposition *in vacuo* proceeds in 99% yield. Labelled

TABLE 1.

Wt. of palladous chloride (mg.) .....	191.2	161.4
Wt. of chlorine (mg.) .....	76.3	64.4
Wt. of chlorine recovered (mg.) (%) .....	75.2 (98.6%)	63.7 (98.9%)

chlorine is readily obtained by dissolution of palladous chloride in aqueous [ $^{36}\text{Cl}$ ]hydrochloric acid to allow exchange of chlorine, careful distillation to dryness of the solution to remove aqueous hydrochloric acid, and subsequent decomposition of the palladous [ $^{36}\text{Cl}$ ]chloride *in vacuo*. It has been established that 97—99% of the chlorine based on the original weight of palladous chloride can be recovered when this procedure is followed. The only by-product is pure aqueous [ $^{36}\text{Cl}$ ]hydrochloric acid of lower specific activity which can be used again.

Auric and platinum chloride also decompose to the metal and chlorine on being heated and have been used to provide a convenient source of a known amount of pure chlorine in an evacuated system.<sup>3</sup> The use of these chlorides in the above procedure is not feasible, however, because of decomposition of the halide during the removal of the hydrochloric acid.

A series of experiments was carried out with various ratios of unlabelled palladous chloride to [ $^{36}\text{Cl}$ ]hydrochloric acid. The specific activity of chlorine resulting could be calculated on the basis of dilution of the original [ $^{36}\text{Cl}$ ]hydrochloric acid activity by known amounts, with complete exchange assumed. The chlorine from each decomposition was recovered and counts of solutions of known concentration were made. Comparison of these figures with the expected values (Table 2) shows that agreement is good. The fact that the observed values tend to be slightly higher than the calculated values probably indicates the presence in the [ $^{36}\text{Cl}$ ]chlorine of a small amount of hydrogen [ $^{36}\text{Cl}$ ]chloride.

TABLE 2.

	Stock HCl	A	B	C	D
Unlabelled Cl (as $\text{PdCl}_2$ ) (mg.) .....		9.90	8.26	8.26	7.31
Labelled Cl (as HCl) (mg.) .....		9.95	11.77	14.49	27.13
Specific activity of mixture (% of original) .....	100	50.1	58.8	63.7	78.8
Observed counts per min. per mg. of Cl * .....	4550	2290	2762	2810	3710
Chemical yield (%) .....		98.6	97.2	92.6	98.7
Observed counts per min. per mg. of Cl, corr. for chemical yield .....		2320	2842	3033	3758
Calc. counts per min. per mg. of Cl .....	(4550)	2279	2678	2900	3585

\* The mg. of chlorine present being calculated on the assumption of 100% yield from the palladous chloride decomposition.

These experiments show that labelling of palladous chloride by exchange with [ $^{36}\text{Cl}$ ]hydrochloric acid and subsequent decomposition of the [ $^{36}\text{Cl}$ ]palladous chloride provides a convenient and reliable method by which [ $^{36}\text{Cl}$ ]chlorine, in known amount and of known specific activity, may be obtained in an evacuated system.

<sup>2</sup> Puche, *Compt. rend.*, 1935, **200**, 1206.

<sup>3</sup> Travers, "Experimental Study of Gases," Macmillan and Co., New York, 1901, p. 47.

The analogous thermal decomposition of labelled palladous iodide has been used previously in these laboratories<sup>4</sup> as a convenient method for the preparation of labelled iodine.

#### EXPERIMENTAL

*Decomposition of Unlabelled Palladous Chloride.*—Palladous chloride (Johnson, Matthey and Co. Ltd.) was dried at 100° for 24 hr. and stored in a desiccator. Samples were weighed into 50 ml. Pyrex distillation flasks, and the necks of the flasks were sealed off above the side arms. Each flask was then fused on to a receiving vessel containing an excess of 0.1M-potassium iodide, this vessel being attached to a high-vacuum system. Greased joints or taps between decomposition flask and receiver were avoided since chlorine attacks tap-grease. After the solutions had been degassed and frozen at -180° the apparatus was evacuated and sealed off beyond each receiving vessel. The palladous chloride samples were subsequently decomposed by heating them with a gas flame to a temperature just below the softening point of Pyrex glass, the chlorine being condensed in the receivers at -180°. After the receivers had been sealed off from the decomposition vessels, the potassium iodide solutions were thawed to room temperature. Reaction of the chlorine with the potassium iodide produced iodine, which dissolved in the excess of potassium iodide present. The liberated iodine, and hence the weight of chlorine collected, was estimated by titration against standard sodium thiosulphate solution. Table 1 shows the results obtained, indicating that 99% of the theoretical yield of chlorine can be recovered.

*Concentration of Stock [<sup>36</sup>Cl]Hydrochloric Acid Solution.*—[<sup>36</sup>Cl]Hydrochloric acid (The Radiochemical Centre, Amersham), of nominal specific activity 0.109  $\mu$ C/mg., was transferred to a standard flask and made up to the graduation mark with distilled water. The chlorine content per ml. of solution was determined gravimetrically by precipitation as silver chloride. The solution contained 9.05 mg. of Cl per ml.

*Decomposition of [<sup>36</sup>Cl]Palladous Chloride.*—Known volumes of the stock [<sup>36</sup>Cl]hydrochloric acid solution were added to weighed amounts of palladous chloride. From the respective weights of labelled and unlabelled chlorine, the diluted activities were calculated (Table 2). The neck of each flask was washed down with distilled water before being sealed off. Samples were gently heated to dissolve the palladous chloride, then slowly ( $\frac{1}{2}$ —1 hr.) evaporated almost to dryness at atmospheric pressure. The distillate is pure [<sup>36</sup>Cl]hydrochloric acid of reduced specific activity, which may be retained for future use. Care is required when the samples are nearly dry to avoid overheating, otherwise slight loss of chlorine may occur. The last traces of water and hydrogen chloride were removed in these experiments by immersing the bulbs of the flasks in an oil-bath at 120° for 4 hr. Any droplets of distillate which appeared in the side-arms were removed by means of tissue. Decomposition of the chloride and recovery of chlorine were carried out as already described. Thiosulphate titration indicated that the yields of chlorine were generally 97—99% (Table 2).

*Counting of [<sup>36</sup>Cl]Chlorine Obtained.*—The active solutions, containing chlorine as chloride ion in presence of iodine and potassium iodide, were made up to a known volume with distilled water, and the activity of 10-ml. portions was determined by normal technique (halogen quenched liquid counter tube). Dilutions of the stock [<sup>36</sup>Cl]hydrochloric acid solution (in presence of the same concentration of potassium iodide) were counted under similar conditions. Values of counts per minute per mg. of chlorine for each sample (corrected for the small amounts of chlorine not recovered) were then compared with the values already calculated for the samples on the basis of dilution of activity. Results are given in Table 2.

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<sup>4</sup> Purkayastha and Martin, *Canad. J. Chem.*, 1956, **34**, 293.