

RADIOCHEMISTRY

Rapid Non-destructive Analysis of Chlorine by Neutron Activation

It is known that 1.0-sec chlorine-38m is formed by neutron irradiation of natural chlorine and that it emits 0.66-MeV γ -ray. So it seems that chlorine can be determined by short-time irradiation with neutrons followed by γ -ray spectrometry. Since the half-life appeared to be too short to bring about precise determinations, we tried at first to observe the precision of the use of ten samples of ammonium chloride, 150 mg each.

They were placed by turns in the nuclear reactor JRR-1 for 2.5 sec to be irradiated with neutrons at a flux of 3×10^{11} neutrons/cm²/sec, cooled for 5 sec, and counted for 1 sec. The counter used was a 2-in. thick, well-type sodium iodide crystal attached to a 256-channel pulse-height analyser. During the counting operation the sample was placed 1 cm above the crystal together with its containers made of polyethylene (inner capsule) and of polyester (outer capsule 'rabbit'). A 2,150-mg/cm² thick aluminium disk was used as an absorber for β -rays from the sample.

On the spectrum obtained the height and the 'width at half-maximum' of 0.66-MeV photopeak were measured, from which peak area was estimated by use of a formula presented by Connally and Leboeuf¹.

Thus, the coefficient of variation of single analyses (or relative standard deviation) was estimated at 14 per cent. Though the coefficient is rather large, it may still be sufficient for the purpose of rapid, non-destructive analysis for chlorine.

Then this method was modified to determine the half-life of chlorine-38m so as to confirm the identification of chlorine, and was applied to samples of bleaching-powder. Ammonium chloride was used as a chlorine standard. The results of the analyses are given in Table 1, and a typical spectrogram in Fig. 1.

Sample	Sample weight used (mg)	Chlorine found (%)
A { No. 1	393.1	30.1
	420.2	31.9
B { No. 1	229.1	27.0
	218.8	29.7

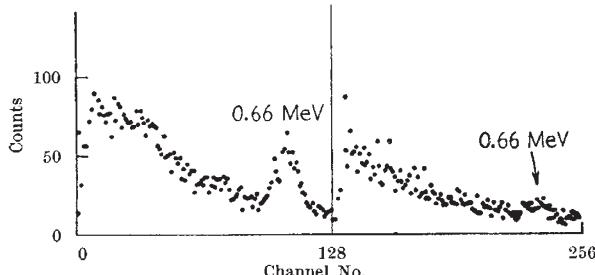


Fig. 1. γ -Ray spectrogram. Sample: 393.1 mg of bleaching powder (sample A, No. 1 in Table 1). Time of irradiation, transfer, first counting, interval, and of second counting are 2.5 sec, 5 sec, 1 sec, 1 sec, and 1 sec, respectively.

It is deduced that the method is favourably applicable to various organic compounds in spite of the relatively low activation-cross-section of chlorine.

It was found that both sodium chloride and potassium chloride can be used as a chlorine standard.

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¹ Connally, R. E., and Leboeuf, M. B., *Anal. Chem.*, **25**, 1095 (1953).

CHEMISTRY

Nature and Reactions of the Reducing Species in Aqueous Solutions irradiated with γ -rays in the Presence of Oxygen

We have previously¹ demonstrated the existence of a dehydrogenating species in de-aerated neutral aqueous solutions of aliphatic alcohols, when these are irradiated with γ -rays. This particular species, produced in a yield of $G=0.5-0.6$ (molecules/100 eV), was assumed to be a hydrogen atom, possibly formed from excited water molecules according to: $H_2O^* \rightarrow H + OH$. A similar conclusion has also been arrived at by Rabani and Stein^{2,3}, using 200-kV X-rays. The identity of the dehydrogenating species as a simple hydrogen atom appears to be supported by kinetic evidence^{2,3} as well as by its reaction with OH^- ions^{4,5}. Other authors have suggested that one may be dealing with a radical pair ($H + OH$) (ref. 6) or an excited water molecule reacting as such^{6,7}. For this, and other, reasons we shall represent this dehydrogenating species as H^α . The major proportion of the reducing species consists of electrons, also described as negative polarons⁸, and represented here as $(H_2O)^-$.

Recently, questions have arisen concerning the existence of H^α in systems containing oxygen^{7,9,10}. In particular, Hummel and Allen¹⁰, in an investigation of the yields of hydrogen on γ -irradiation of aqueous ethanol solutions containing oxygen, concluded that there was a competition between ethanol and oxygen for a reducing species, but were unable to decide whether this was $(H_2O)^-$ or a hydrogen atom. Somewhat similar effects in oxygenated lactate solutions, irradiated with 200-kV X-rays, have been observed by Johnson¹¹. We have re-investigated this effect using oxygenated solutions of sodium formate. This particular organic solute was selected because: (a) its reaction with the negative polaron does not apparently lead to formation of hydrogen¹²; (b) the formate ion has a relatively high reactivity towards H^α (ref. 13) as well as to externally generated hydrogen atoms¹⁴. Solutions of formate of varying concentrations ($10^{-3}-5 \times 10^{-1}$ M) were saturated with oxygen (1 atm.) and irradiated with cobalt-60 γ -rays. The yields of hydrogen were determined mass spectrometrically, after removal of excess oxygen with yellow phosphorus, this method giving results accurate to about ± 5 per cent. The results (Table 1) show that the yields of hydrogen increase with increasing formate concentration, indicating a reaction involving H^α and not $(H_2O)^-$. Furthermore, the results follow simple competition kinetics leading to a value of $G(H^\alpha) = 0.75 \pm 0.1$, in fairly good agreement with that obtained in de-aerated systems. Thus, both $(H_2O)^-$ and H^α can undergo reactions in the presence of oxygen, in disagreement with the statement of Hayon⁷ that only $(H_2O)^-$ reacts under these conditions.

Over the range of formate concentration where $G(H_2)$ increases markedly, the yield of hydrogen peroxide changes relatively little (Table 1), a situation similar to that observed in the ethanol-oxygen system¹⁰. This would be expected if H^α is, in fact, a hydrogen atom, reacting competitively, according to: $H + HCOO^- \rightarrow H_2 + COO^-$ and $H + O_2 \rightarrow HO_2$, since the reaction with formate will be followed by, $COO^- + O_2 \rightarrow CO_2 + O^-$. Given the accepted mechanism for the radiolysis of aqueous oxygenated formate solutions¹⁵ and assuming $G_{H_2}^w = 0.39$, the value of $G(H_2)$ at the lowest formate concentrations, the results presented here lead to values of $G((H_2O)^-) = 2.3 \pm 0.1$ and $G(H^\alpha) = 0.75 \pm 0.1$. In certain other aqueous systems, for example, in solutions containing $N_2O +$ alcohol¹³, or $CO_2 +$ alcohol¹⁶, $G(H^\alpha)$ and $G((H_2O)^-)$ have been directly measured. The values obtained for $G(H^\alpha)$ are in agreement with that obtained here. However, values of $G((H_2O)^-)$ up to 2.9 have been observed.