more, since only (DPPH)OH and (DPPH)H addition products have been identified, and not even one product isolated in measurable amounts gave mass higher than 412 in the mass spectrum, any reaction between RO· or ROO· and DPPH may be considered as negligible.

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Reliability of the Thiobarbituric Acid Test in the Presence of Inorganic Iron

IN recent years, the validity of the 2-thiobarbituric acid (TBA) test for the determination of oxidative deterioration in animal and plant tissues, or their food products, has been challenged. However, since most authors prefer to use their own modification of a TBA test, comparison of results obtained at different laboratories is virtually impossible. Considerable confusion is therefore created by these claims, rather than clarification of the subject.

It has been demonstrated time and again that the TBA test is one of the most reliable tests for measuring the extent of oxidative deterioration in substrates containing unsaturated fatty acids. Only in the case of measurements involving either the initial or the very late stages of oxidation is the TBA test not very valid.

The TBA test measures the amount of malonaldehyde which is formed during the oxidation of the unsaturated fatty acids[1]. Malonaldehyde is primarily produced from the oxidative cleavage of 2-enals and 2,4-di-enals[2], which in turn are products of the breakdown of hydroperoxides[3]. Therefore no malonaldehyde is expected to be found at the early stages of oxidation, during which the rate of decomposition of hydroperoxides is negligible.

On the other hand, it has been shown conclusively that malonaldehyde does not accumulate as a stable end product during the oxidation of unsaturated fatty acids, but that it is destroyed at the very late stages of oxidation[4]. It is not, therefore, surprising that malonaldehyde cannot be found after an 18 h oxidation of methyl linolenate under ultra-violet radiation at 45° C (ref. 5).

It has been reported recently that inorganic iron present in the medium during the performance of the TBA test gives much higher results, in comparison with tests during which no iron is present[6]. Because of the extremely high concentration of free iron used in this investigation (10,000–100,000 p.p.m.), which is scarcely to be expected in any animal or plant, we have re-investigated the effects of iron on the TBA test.

The TBA methods used for assay were those described in previous publications[7,8].

100–5,000 p.p.m. of ferric ions were added before or after distillation to 0·1–1 g of methyl linolenate, rape seed, soyabean or groundnut oil, which were oxidized to a peroxide value (P.V.) from 1 to 40 mmoles/kg[9]. After the TBA test was carried out on a portion of the distillate[7,8] and under a variety of conditions, including heating at 20° C or 100° C, in water or 90 per cent acetic acid solution, the absorbance of all samples was measured at 530 mμ in a 'Unicam' *SP* 800 recording spectrophotometer. In no case was any significant difference in absorbance observed between the samples containing iron and the appropriate blanks. However, when 10,000–100,000 p.p.m. of ferric ions were added to the same oils and the experiments were repeated, significant increase in absorbance was observed in the samples containing iron before distillation, for example, the absorbance was increased from 0·9 to 2·8 by the presence of ferric ions. This increase was directly proportional to the P.V. of the substrate before the test, and it was much lower when the test was performed in water at 20° C than in acid at 100° C.

The effects of iron on TBA and the TBA-malonaldehyde complex[10] were investigated because of suggestions that the increased absorbance may be due to formation of metal chelates.

Ferric ions were added to 1×10^{-2} M TBA or 5×10^{-5} M TBA-malonaldehyde solutions in water or acetic acid, which were then heated to 20° C or 100° C for 15 h or 40 min respectively. In all cases, even when the concentration of iron was as high as 300,000 p.p.m., no difference in absorbance at 530 mμ was observed from that of the blanks. It is, therefore, concluded that inorganic iron does not form complexes with the above compounds, or if it does, the change in absorbance at 530 mμ is negligible and it does not alter the results of the TBA test.

The effects of iron on malonaldehyde have been investigated previously[11]. It has been shown that although malonaldehyde chelates iron, the recovery by distillation is not affected by iron chelation even with 10 : 1 ratios of iron to malonaldehyde.

The results of the experiments show that ferric ions present in a medium up to a concentration of 5,000 p.p.m. do not alter the results of the TBA test. Higher concentrations of iron induce changes which may be attributed to an acceleration of the decomposition of malonaldehyde precursors by the iron[12] rather than to formation of iron chelates. Since the changes induced by iron take place almost exclusively when the test is performed in acid medium and at high temperatures, the use of milder conditions during the performance of the TBA test[8] is recommended.

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Exchange Reactions in the Radiolysis of Adsorbed Hydrocarbons

THE radiolysis of hydrocarbons adsorbed on silica gel was first investigated by Caffrey and Allen[1] and later by Sutherland and Allen[2], who found that the hydrogen yield was several times larger than that expected from the amount of energy absorbed directly by the hydrocarbon itself. In an attempt to investigate more thoroughly the role of the silica gel, we have studied the radiolysis of *cyclo*hexane-d_{12} adsorbed at low coverages on silica gel.

Silica gel (50–60 mesh) was obtained from Analabs, Inc., Hamden, Connecticut, and had a surface area of