ENTHALPIMETRIC DETERMINATION OF THE IODINE VALUE OF SOME EDIBLE OILS AND FATS

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A simple, rapid and accurate direct injection enthalpimetric (DIE) method has been developed for the determination of the iodine value of some commercial edible oils. A significant heat pulse of halogen addition reaction of the double bonds of unsaturated fatty acid esters in the oils is produced by injecting a solution of iodine monochloride into the sample solutions. The method is calibrated against real samples and the standard compounds (oleic, linoleic and linolenic acids) whose iodine values have been determined by a standard method. Once calibrated, the proposed method can be operated routinely by semi-skilled personnel. The method is sensitive and give results as acceptable as those obtained by standard methods. The main advantages of the method are those of time and cost of analysis and the potential of the enthalpimetric method for automation.

The "iodine value" of oils and fats is one of the most valuable and widely used characteristic for the evaluation and differentiation of these substances representing as it does a measure of the degree of unsaturation. For some time the determination of this value has been of universal importance, and there is, at present, a steadily increasing demand for a simple and rapid method which will be adaptable for routine work, will require no special apparatus and be relatively economical in use. In spite of this, no single, rapid and accurate method which will give consistent results on all types of oil has been previously reported.
A number of methods have been devised for the determination of the iodine value, and it is well known that all the methods do not yield identical results. Although many halogen absorption methods are available, only those using iodine monochloride (Wijs method) [1] and iodine monobromide (Hanus method) [2] are widely used, even though these methods are time consuming. Catalysts have been used to decrease the long time required for complete absorption and reaction of the halogen. Mercuric acetate has been used in the Wijs procedure [3-5]. Benham and Klee [6] modified the Rosenmund Kuhnenn method [7] using this reagent. Another reagent, hypochlorous acid was introduced [8] to reduce the time of reaction, and was used [9] for determining the iodine value of oils with conjugate unsaturation, commercial bleaching solutions were later introduced [10] as reagents.

Since the halogen addition reaction generally releases a significant amount of heat, and the reaction could be forced to occur immediately by the use of a large excess of reagent, the Direct Injection Enthalpimetric (DIE) method [11] potentially provides an ideal technique to satisfy the problem of providing a rapid method of analysis. The reported potential uses of iodine monochloride in solution thermal chemistry [12], indicate that it should be useful for the rapid determination of the amount of unsaturation in oils and fats.

Experimental

Apparatus

The basic circuit of the electrical bridge system and the reaction vessel have been previously reported [13, 14].

Reagents

All reagents used were of analytical-reagent grade.

For determining the iodine value by standard Wijs and Hanus methods

Carbon tetrachloride was used to dissolve the samples. Solutions of 0.5 \( M \) iodine monochloride and of iodine monobromide and of 5% w/v mercuric acetate in glacial acetic acid were used as iodinating agents and catalyst respectively. The unabsorbed iodine was titrated using solutions of 10% w/v potassium iodide and of 0.1 \( N \) sodium thiosulphate.