

Olive Oil Quality Control by Using Pyrolysis Mass Spectrometry and Artificial Neural Networks

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The adulteration of food-stuffs is a major problem from several points of view which necessitates the implementation of rapid and accurate methods for its detection. This article reports the application of Curie-point pyrolysis mass spectrometry (PyMS) to the recognition of a variety of extra virgin olive oils, and some of the same oils which had been deliberately adulterated with other lower-grade seed oils. Artificial neural networks (ANNs) were trained successfully to distinguish (the pyrolysis mass spectra of) extra virgin oils from adulterated olive oils. We consider that the combination of PyMS and ANNs constitutes a powerful and novel approach to the detection of adulterations in olive oil and food generally.

mass spectrometer can then be used to separate the components of the pyrolysate on the basis of their mass-to-charge ratio (m/z) so as to produce a pyrolysis mass spectrum, which can then be used as a «chemical profile» or fingerprint of the complex material analysed, and the combined technique is then known as pyrolysis mass spectrometry (PyMS) (Meuzelaar et al., 1982; Aries et al., 1986).

Virgin olive oil is the oil extracted by purely mechanical means from sound, ripe fruits of the olive tree (*Olea europaea* L.). Such oils with a free fatty acid content (in terms of oleic acid) below 1% are known as «extra virgin», whilst oils with good flavour but greater acidity are commonly called «virgin» or «ordinary». Lower grades in-

clude oils that have a high acidity and flavour and/or aroma defects which are corrected by refining; these are known as «lampante» oils. Olive oil contributes significantly to the nutritional and health benefits of Mediterranean-type diets and, uniquely among vegetable oils, the flavour of olive oil is best enjoyed without refining. Olive oil therefore commands a higher price than do other vegetable oils, and these and other properties mean that there is a great temptation to adulterate olive oils with other seed oils (Kiritakis and Marakakis, 1991).

A number of methods have been proposed for the detection of olive oil adulteration, for example chromatographic (Kapoulas and Passaloglou-Emmanoulidou, 1981), near infrared (Sato et al., 1991) and

INTRODUCTION

There is an ongoing requirement for methods which might be exploited for the rapid characterisation of biological systems, for instance in determining whether a particular food-stuff has the provenance claimed for it or whether it has been adulterated. We here describe a novel approach to the solution of this problem, and its application to the distinction between extra virgin and adulterated olive oils.

Pyrolysis is the thermal degradation of complex material in an inert atmosphere or a vacuum. It causes molecules to cleave at their weakest points to produce smaller, volatile fragments called pyrolysate. A

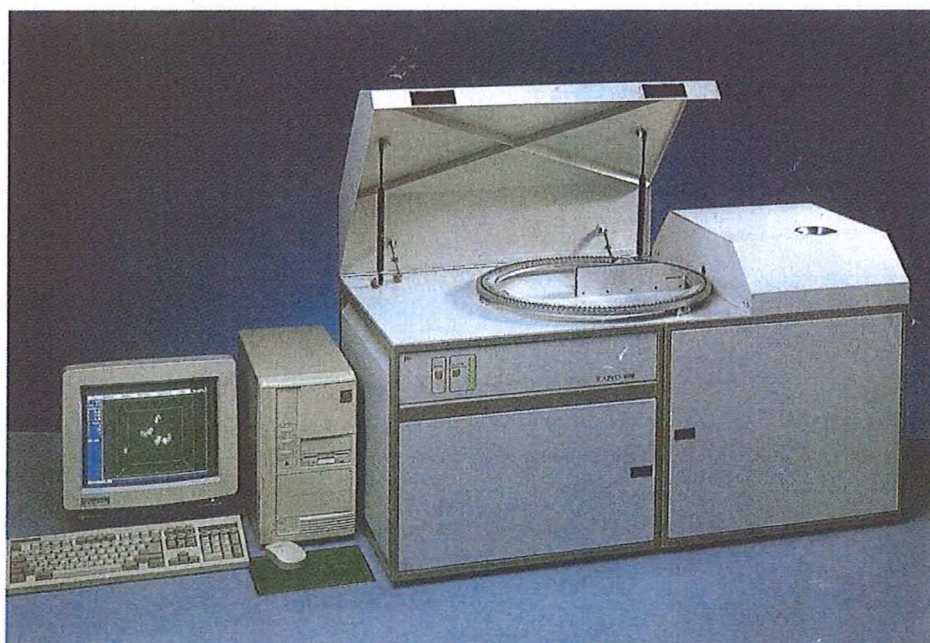


Figure 1. The Horizon Instruments pyrolysis mass spectrometer

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METHODS AND RESULTS

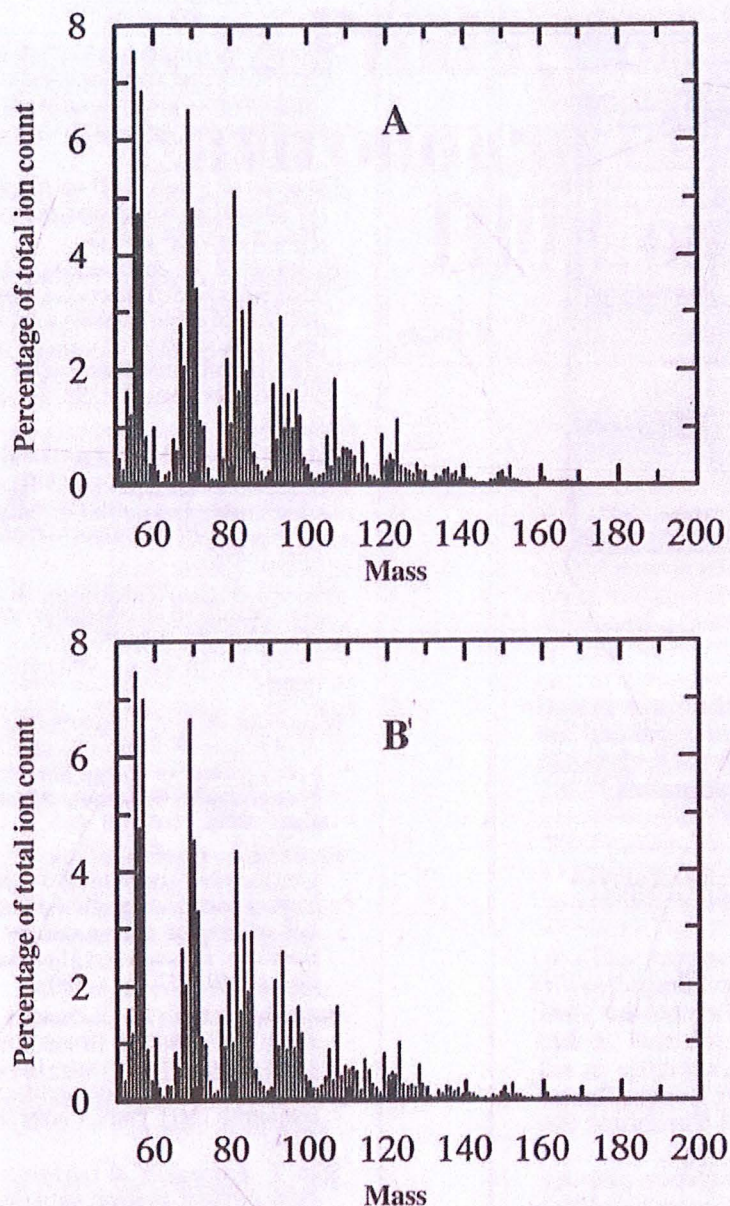


Figure 2. Normalised pyrolysis mass spectra of an extra virgin olive oil (A) adulterated with 5% sunflower oil (B).

UV spectrophotometric methods (Passaloglou-Emmanouilidou, 1990), although none appears to have found widespread usage or all-round effectiveness.

Chemometrics is the discipline concerned with the application of statistical and mathematical methods to chemical data (Massart et al., 1988). A related approach is the use of (artificial) neural networks (ANNs), which can be considered as collections of very simple «computational units» which can take a numerical input (pyrolysis mass spectra)

and transform it into an output (i.e., whether the oil is of virgin quality or adulterated) (Rumelhart et al., 1986). The great power of neural networks stems from the fact that it is possible to «train» them. When training is completed the ANN may then be exposed to «unknown» pyrolysis mass spectra and will then «immediately» output the status of the oils. If the outputs from the previously unknown inputs are accurate, the trained ANN is said to have generalised.

The protocol of the experiment was as follows (Goodacre et al., 1992). Two sets of samples were prepared, one consisting of 12 samples of various extra virgin olive oils and the other of 12 samples variously adulterated with 5-50% of soya, sunflower, peanut, corn or refined olive oil. The experiment was performed double-blind, such that the identities of the second set were not known. PyMS was performed at 530°C using a Horizon Instruments machine (see Fig. 1) as described by Aries et al. (1986); two typical spectra are shown in Fig. 2, where it is obvious that it is not at all easy to distinguish them by eye.

ANN analyses were carried out using a user-friendly, neural network simulation program, NeuralDesk (Fig. 3), which runs under Microsoft Windows/3.1 on an IBM-compatible PC. To ensure maximum speed, we used an accelerator board for the PC (NeuSprint), based on the AT&T DSP32C chip and obtained from the same source, which effects a speed enhancement of some 100-fold, permitting the analysis (and updating) of some 400,000 weights per second. We trained an ANN consisting of an input layer of the 150 normalised averaged ion intensities from the pyrolysis mass spectra of the first set of oils with mass range 51-200, and 1 hidden layer of 8 nodes, using the standard back-propagation algorithm (Rumelhart et al., 1986), coding virgin oils as 1, non-virgin as 0. The effectiveness of training was expressed in terms of the root mean squared (RMS) error between the actual and the desired outputs over the entire training set. When training had ceased (i.e., an RMS error of 0.001 had been attained), the trained ANN was interrogated with the normalised averaged ion intensities of the pyrolysis mass spectra from the second set of oils (the unknowns). When the code was broken, it transpired that the ANN had correctly assessed each oil. In a typical run, the

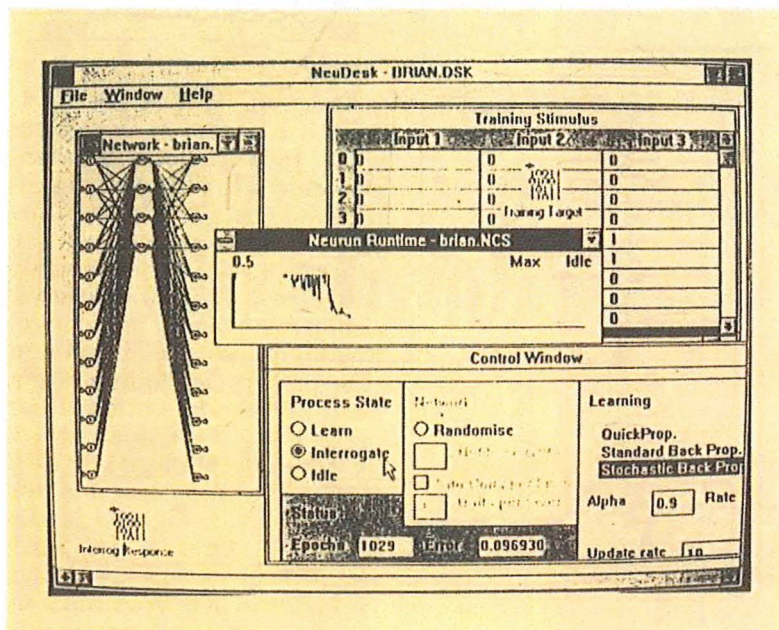


Figure 3. The Neural Computer Sciences NeuralDesk artificial neural network simulation program.

virgins were assessed with a code of 0.99976 ± 0.000146 , (range 0.99954 - 1.00016) and the non virgins with a code of 0.001079 ± 0.002838 (range 0.00026 \pm 0.01009).

CONCLUSIONS AND ADVANTAGES OF THE METHOD

PyMS has major advantages of speed (the typical sample time is less than 2 mins) and automation, which allows approximately 300 samples to be analysed daily. Furthermore, after the initial outlay of some £50,000 on the British-made system, running costs are relatively cheap, typically about £1 per sample. The discriminating power of the approach is enormous, since if each (normalised) mass is accurate to within 10% there are 10150 possible pyrolysis mass spectra, and all biological material may be pyrolysed in the way described. The study reported here clearly shows that the use of pyrolysis mass spectrometry and artificial neural networks was able rapidly and accurately to assess the contamination of virgin olive oils with 5-50% corn, peanut, soya, sunflower oil, or refined olive oil. In conclusion, the combination of

these two techniques constitutes a novel, powerful and universal approach to the detection of food adulteration.

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