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# Concentrations of metals in vegetable edible oils

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Concentrations of Na, K, Ca, Mg, Cu, Zn and Fe as well as the indices of acidity and peroxides have been determined in several Spanish edible oils. For Cu and Fe, respectively, 18·3% and 2·8% of the samples showed higher values than the maximum permitted by FAO/WHO. However, there were no samples that exceeded the maximum values established by the Spanish directorate for these two metals. Maximum values for the indices of acidity and peroxides established by the Spanish directorate were exceeded in 17% and 21% of the samples overall. Olive oil had a higher number of samples that exceed the maximum values of the Spanish directorate than other analysed oils. The ratio Na/K was always higher than unity, which means that the oils had been subjected to a refinement process. Strong correlations between Na and K and between Ca and Mg were found in all the types of oil studied. Also, moderate correlations between the acidity index and the concentration of Fe, and between the indices of acidity and peroxide, have been observed.

## INTRODUCTION

The presence of metals in vegetable oils is due to two factors: their contents in the starting raw materials or contact with the manufacturing or storage equipment. Some metals, such as Cu and Fe, are particularly harmful, since they may accelerate oxidation reactions at concentrations of a few μg/g, which are involved in rancidity processes (Robinson, 1960; Fedelli *et al.*, 1973; Hardisson *et al.*, 1986; Salcedo, 1991). A comparison, between two oil-producing systems, of the content of Fe and Cu of virgin olive oil has been carried out. Higher Fe and Cu levels were found with the old processing system (classical press and super press) than with new systems (continuous decanter and Sinolea) (Nergiz & Unal, 1990). Also, the extractive capacity of peptic acid (Ivanov *et al.*, 1990) as well as membrane extraction (Keurentjes *et al.*, 1990) have been developed to remove metals from edible oils. Thus, the autoxidative stability was increased. In the final stages, the auto-oxidation of oils produces oxidative compounds such as peroxides, aldehydes, ketones, acids and epoxides, among others. These compounds may develop pathological effects on the digestive system, but also interact with components of the foods such as proteins and pigments, sensitizing the action of certain carcinogens. Hence, it is important to monitor and control the presence of elements in the oil samples .

Several spectrophotometric, emission spectrographic, polarographic, and chromatographic methods have been reported in the literature for determining heavy metals in edible oils (Mehlenbacher, 1979), but atomic absorption spectrometry (AAS) (flame or electrothermal) is the most selective and sensitive technique available for these determinations. Sample treatment is the most decisive step in the AAS determinations (Salcedo, 1991). There are three important methods of sample treatment of vegetable oils: ashing, extraction and simple dilution. Wet ashing (Elson *et al.*, 1979) causes no losses of inorganics but the risk of contamination and explosion (if perchloric is used) is higher than in the other methods. Also, wet ashing produces changes in the original medium which can diminish the accuracy of the final measure (Torre *et al.*, 1990). Oil samples tend to pull during carbonization, so careful control of the muffle temperature programming is indispensable (Alvarez *et al.*, 1986; Persmark & Toregard, 1971; Ooms & Van Pee, 1983). Char-ashing permits almost complete recovery of most of metals (Evans *et al.* 1971; Hvolby, 1971; Black, 1975; Tsai *et al.*, 1978). However, some metals such as Cd or Zn may be partially lost by volatilization (Black, 1975). Char-ashing is a sensitive and useful technique, but takes too long (Evans *et al.* 1971; Persmark and Toregard, 1971; Black, 1975; Jacobs & Klevay, 1975). Extraction methods suffer from incomplete recoveries due to a deficient break up of the organometallic compounds in oil (Ooms & Van Pee, 1983). However, metal recoveries in extraction methods were slightly lower than in char ashing methods (Jacob & Klevay, 1975). Acid EDTA extraction of oils requires 4 h, and several samples can be analysed using simultaneous reflux extractions (Jacob & Klevay, 1975; Torre *et al.*, 1990). Diluting the sample with methyl-isobutyl-ketone (MIBK) (List *et* *al.*, 1971) or other solvents (Hon *et al.*, 1980; Minganti *et al.*, 1989) reduces the metal concentration and needs a metal-free base oil or the use of a standard addition method for matrix. But this sample treatment is fast and simple, and reduces the manipulation of the oil, minimizing its possible contamination (Persmark & Toregard, 1971; Ooms & Van Pee, 1983). Recently, a simple procedure, based on the flow-injection standard additions, has been developed for determination of Cu and Fe without dilution in edible oils by flame atomic absorption spectrometry.

In the present work, determinations of Na, K, Ca, Mg, Cu, Zn and Fe, and of the indices of acidity and peroxides have been carried out in order to provide some information about the quality of several Spanish edible oils. Moreover, the metal concentrations have been correlated among one another and with the indices of acidity and peroxides.

## MATERIALS AND METHODS

### Apparatus

- Pye Unicam SP-1900 and Perkin-Elmer 3030 B (deuterium background corrector) atomic absorption spectrophotometers, provided with Na, K, Ca, Mg, Fe, Cu and Zn hollow cathode lamps. The main instrumental parameters are summarized in Table 1. No mutual interferences existed in the ranges of concentration observed (Pinta, 1971; Hardisson, 1984).
- Heraeus KR-170 furnace.
- Digital VAX/VMS 11/780 (V.4.7).
- Milli-Q OM-140 water system.

### Reagents and solutions

- 1000 ppm Na, K, Ca, Mg, Fe, Cu, and Zn Fisher certified solutions for A.A.S.
- Standard solution of potassium hydroxide, 0·5 N.
- Standard solution of sodium thiosulphate, 0·01 N.

Analytical reagent-grade chemicals and Milli-Q water were used.

### Samples

One hundred and twenty samples of the main Spanish brands of edible vegetable oils (rapeseed, seed, corn, sunflower, soya and olive) were purchased in supermarkets of Santa Cruz de Tenerife during 1988 and 1989. The analyses were performed after homogenization of the contents of each bottle.

### Analytical methodologies

Metals (dry ashing): 25–30 g of oil sample was weighed into a porcelain capsule, which capsule was then introduced into a muffle furnace at ≈300°C until the sample stopped smoking. Ashing was continued at ≈400°C for 2 h and completed at 500 ± 25°C overnight (to white ash). After cooling, ash was dissolved in 5 ml of HCl (1 + 1), warmed in a water bath and transferred into a 25 ml volumetric flask. The metallic concentrations of these solutions were measured by A.A.S. using the described conditions (Table 1).

**Table 1. Instrumental conditions for AAS determination of the studied metals**

| Metal | $\gamma$ (nm) | Slit (nm) | Lamp current (mA) | Height burner (cm) |
|---|---|---|---|---|
| Na | 589·0 | 1·4 | 7 | 1·0 |
| K | 766·5 | 1·4 | 7 | 1·0 |
| Ca | 422·7 | 1·4 | 8 | 1·0 |
| Mg | 285·2 | 0·7 | 3·5 | 1·0 |
| Fe | 248·3 | 0·7 | 3·5 | 1·0 |
| Cu | 324·7 | 0·7 | 6 | 1·0 |
| Zn | 213·9 | 0·2 | 10 | 1·0 |

In all cases, the flues of air and acetylene were 5·0 and 1·0 litres/min. respectively.

Standard methods recommended for the Spanish directorate (Metodos Oficiales, 1974) have been used for the determination of acidity and peroxide values.

## RESULTS AND DISCUSSION

The method described in Material and Methods (Method 1) has been compared with the Spanish Official Method (Method 2) which is similar to that of IUPAC (1979). For all the metals analysed, no significant differences ($p > 0·1$) were observed between the two methods (Table 2). Since Method 1 was simpler and faster than Method 2, the former has been applied to the samples of trade oils analysed in this work. Mean, maximum and minimum values and the coefficients of variation for the metal concentrations and quality indices studied are presented in Table 3. The overall results of the analysed samples and each type of oil separately have been considered. There are no significant differences ($p > 0·1$) among the mean concentrations of analysed metals with respect to different types of oil. None of the samples surpassed the maximum legislated for Fe and Cu of 10 and 0·4 μg/g, respectively quoted in the Spanish directorate (B.O.E., 1983). Mean values obtained in this work for Cu and

**Table 2. Comparison of the described method (Method 1) with the Spanish Official Method (Method 2).**

| Metal | Method 1 | Method 2 | $p$ |
|---|---|---|---|
| Zn | 0·089 ± 0·011 | 0·090 ± 0·006 | >0·5 |
| Cu | 0·025 ± 0·006 | 0·025 ± 0·006 | >0·05 |
| Fe | 0·99 ± 0·08 | 1·02 ± 0·10 | >0·2 |
| Ca | 1·13 ± 0·17 | 1·27 ± 0·11 | >0·1 |
| Mg | 0·25 ± 0·07 | 0·23 ± 0·07 | >0·5 |
| Na | 3·34 ± 0·59 | 3·25 ± 0·57 | >0·5 |
| K | 0·94 ± 0·09 | 0·82 ± 0·08 | >0·2 |

Adopted null hypothesis has been that there are no differences between analytical methods; degrees of freedom = 20.

**Table 3. Mean, maximum and minimum concentrations and coefficients variation for the overall analysis and for each type of oil analysed**

| ELEMENT | | Total (109)[a] | Rapeseed (20)[a] | Seeds (20)[a] | Sunflower (18)[a] | Corn (21)[a] | Soya (8)[a] | Olive (22)[a] |
|---|---|---|---|---|---|---|---|---|
| Fe | Mean | 0·68 | 0·62 | 0·54 | 0·55 | 0·64 | 0·59 | 1·01 |
| (μg/g) | Maximum | 2·20 | 1·56 | 1·15 | 1·31 | 1·25 | 0·76 | 2·20 |
| | Minimum | 0·22 | 0·22 | 0·31 | 0·27 | 0·22 | 0·38 | 0·49 |
| | C.V. | 51·3 | 50·1 | 37·4 | 53·6 | 44·4 | 23·7 | 42·3 |
| Cu | Mean | 0·07 | 0·06 | 0·07 | 0·06 | 0·07 | 0·08 | 0·09 |
| (μg/g) | Maximum | 0·33 | 0·18 | 0·27 | 0·19 | 0·17 | 0·12 | 0·33 |
| | Minimum | 0·02 | 0·02 | 0·02 | 0·03 | 0·02 | 0·04 | 0·03 |
| | C.V. | 69·9 | 65·6 | 79·2 | 67·7 | 53·4 | 42·1 | 81·1 |
| Zn | Mean | 0·17 | 0·19 | 0·12 | 0·16 | 0·20 | 0·15 | 0·17 |
| (μg/g) | Maximum | 0·70 | 0·47 | 0·17 | 0·33 | 0·70 | 0·27 | 0·43 |
| | Minimum | 0·04 | 0·10 | 0·04 | 0·08 | 0·05 | 0·08 | 0·06 |
| | C.V. | 53·6 | 44·5 | 27·2 | 39·9 | 69·2 | 34·2 | 53·3 |
| Na | Mean | 2·23 | 2·06 | 2·57 | 2·50 | 2·00 | 2·28 | 2·07 |
| (μg/g) | Maximum | 7·04 | 4·85 | 5·23 | 7·04 | 4·79 | 4·85 | 4·41 |
| | Minimum | 0·45 | 1·21 | 0·45 | 1·04 | 0·82 | 1·77 | 0·83 |
| | C.V. | 49·3 | 39·8 | 46·9 | 60·7 | 52·2 | 46·2 | 42·4 |
| K | Mean | 0·56 | 0·45 | 0·57 | 0·57 | 0·48 | 0·51 | 0·74 |
| (μg/g) | Maximum | 2·57 | 1·84 | 1·77 | 2·13 | 1·94 | 1·90 | 2·57 |
| | Minimum | 0·06 | 0·15 | 0·10 | 0·07 | 0·06 | 0·25 | 0·10 |
| | C.V. | 103 | 83·0 | 88·4 | 122 | 114 | 112 | 106 |
| Ca | Mean | 2·99 | 4·05 | 2·40 | 2·25 | 3·50 | 2·61 | 2·44 |
| (μg/g) | Maximum | 14·3 | 14·3 | 5·72 | 6·77 | 10·9 | 5·21 | 6·32 |
| | Minimum | 0·22 | 0·37 | 0·23 | 0·22 | 1·06 | 1·71 | 0·96 |
| | C.V. | 83·5 | 101 | 71·2 | 70·2 | 80·1 | 31·8 | 54·3 |
| Mg | Mean | 1·11 | 3·04 | 0·49 | 0·62 | 1·18 | 0·57 | 0·43 |
| (μg/g) | Maximum | 22·5 | 22·5 | 1·39 | 4·28 | 16·0 | 1·62 | 1·20 |
| | Minimum | 0·06 | 0·11 | 0·13 | 0·06 | 0·09 | 0·28 | 0·14 |
| | C.V. | 290 | 206 | 77·5 | 184 | 288 | 89·5 | 68·9 |
| A | Mean | 0·29 | 0·15 | 0·17 | 0·37 | 0·31 | 0·13 | 0·48 |
| | Maximum | 2·55 | 0·36 | 0·52 | 2·55 | 0·52 | 0·22 | 1·33 |
| | Minimum | 0·01 | 0·04 | 0·01 | 0·02 | 0·03 | 0·01 | 0·05 |
| | C.V. | 114 | 77·4 | 85·5 | 167 | 37·2 | 61·1 | 63·9 |
| P | Mean | 7·36 | 4·46 | 6·03 | 9·39 | 6·64 | 5·31 | 11·0 |
| | Maximum | 34·8 | 16·0 | 16·1 | 26·6 | 34·8 | 7·48 | 21·4 |
| | Minimum | 0·85 | 1·42 | 1·05 | 3·62 | 0·85 | 2·20 | 2·05 |
| | C.V. | 79·2 | 83·1 | 77·7 | 66·8 | 105 | 33·3 | 53·5 |

[a] Number of samples analysed.
A = Acidity (mg KDH/g), P = Peroxide value (mEqO$_2$/kg).
C.V. = Coefficient of variation of Pearson.

Fe are lower than the maximum values recommended for FAO/WHO (Codex Alimentarius Commission, 1978) (0·1 μg/g for Cu and 1·5 μg/g for Fe), but, 18·2% (20 samples) and 2·7% (3 samples) surpassed these values for Cu and Fe, respectively. Among heavy metals, Fe is the element found in the greatest amount, and Cu the element present at the smallest concentrations. This order is maintained in the range of concentrations and coefficients of variation. Olive oil had higher mean concentrations and ranges for Fe and Cu than the remaining oils, i.e. between similar mean concentrations. Corn oil had the highest mean value for Zn, followed by rapeseed oil. Na presents a mean concentration and range higher than those observed among the heavy metals and approximately four times higher than those of K. However, the coefficient of variation for Na is practically half of that one found for K, indicating that K is submitted to a greater relative variability than Na. Ca is found at higher concentration than Mg and Na and has a mean concentration roughly twice that of K. However, Mg shows the widest range and coefficient of variation, which is clearly higher than those we have seen in the remainder of the metals and indices studied. For Ca and Mg the rapeseed oil has the highest mean values; lower mean values are seen in sunflower and olive oils.

Table 4 shows the metal concentrations reported in the main papers found in the literature in order to compare them with our data. Some authors (Evans *et al.*, 1971; Nash *et al.*, 1983; Ooms & Van Pee, 1983) have found mean values for heavy metals (Fe, Cu and Zn) in different types of commercial oils lower than

Table 4. Concentrations (μg/g) of metals in some vegetable oils

| Reference (year) | Analytical method | Type of oil | Na | K | Ca | Mg | Fe | Cu | Zn |
|---|---|---|---|---|---|---|---|---|---|
| Oome and Van Pee (1983) | Char ashing FAAS | Corn | 1·220 | 0·972 | — | — | 0·154 | 0·015 | 0·005 |
| Carbonell *et al.* (1991) | Char ashing FAAS | Olive[a] | — | — | — | — | 27 | 0·90 | — |
| | Flow injection FAAS | Olive[a] | — | — | — | — | 28 | 1·13 | — |
| Evans *et al.* (1971) | Char ashing EAAS | Soybean salad | — | — | — | — | 0·082 | 0·025 | — |
| Black (1975) | Char ashing FAAS | Soybean[a] | 1·51 | 157 | 9·1 | 44·3 | 1·78 | 0·051 | 1·27 |
| | | | 1·90 | 149 | 10·0 | 47·0 | 1·57 | 0·040 | 1·64 |
| | | | 1·19 | 255 | 11·4 | 49·7 | 6·54 | 0·102 | 2·53 |
| | Direct aspiration FAAS | Soybean[a] | 1·33 | 177 | 19·2 | 45·0 | 1·73 | 0·037 | 1·47 |
| | | | 1·92 | 174 | 20·5 | 47·5 | 1·63 | 0·027 | 1·92 |
| | | | 0·96 | 255 | 21·2 | 49·5 | 6·68 | 0·087 | 2·82 |
| | Carbon rod EAAS | Soybean[a] | 1·17 | 144 | 27·5 | 40·0 | 1·78 | 0·047 | 1·80 |
| | | | 1·35 | 130 | 31·4 | 46·3 | 1·62 | 0·026 | 1·92 |
| | | | 0·88 | 226 | 28·7 | 40·1 | 6·61 | 0·069 | 2·92 |
| Fedelli *et al.* (1973) | ·Dilution MIBK FAAS | Soybean + rapeseed | 0·31 | — | 0·36 | 0·042 | 0·22 | 0·06 | — |
| | | Olive | 0·60 | — | 1·26 | 1·080 | 0·32 | 0·06 | — |
| | | Sunflower | 0·87 | — | 0·47 | 0·051 | 0·57 | 0·05 | — |
| | | Peanut | 1·14 | — | 0·79 | 0·188 | 0·35 | 0·05 | — |
| Nash *et al.* (1983) | Dilution MIBK EAAS | Salad | — | — | — | — | 0·214 | 0·026 | — |
| | Add. Stand. EAAS | Salad | — | — | — | — | 0·348 | 0·036 | — |
| Solines *et al.* (1985) | Dilution MIBK EAAS | Olive | 0·37 | 0·66 | 0·22 | — | — | — | — |
| | | Olive[a] | 0·36 | 9·22 | 1·32 | — | — | — | — |
| Hon *et al.* (1980) | Diluting propionic acid EAAS | Corn | — | — | — | — | 1·50 | — | — |
| | | Peanut | — | — | — | — | 1·43 | — | — |
| | | Salad | — | — | — | — | 0·59 | — | — |
| | | Vegetable | — | — | — | — | 1·86 | — | — |
| Elson *et al.* (1979), 1981) | Digestion EAAS(Cu) FAAS(Zn) | Rapeseed | — | — | — | — | — | 0·04–0·23 | 2·7–64·9 |
| Rabescall *et al.* (1985) | Char ashing FAAS | Olive | — | — | — | — | 1·69 | 0·23 | — |
| Reith *et al.* (1974) | Char ashing FAAS | Vegetable | — | — | — | — | — | — | 0·3 |
| Schütze and Müller (1978) | Dilution EAAS | Vegetable | — | — | — | — | 0·92 | 0·065 | 0·068 |
| Results from present study | Char ashing FAAS | Rapeseed | 2·06 | 0·45 | 4·05 | 3·04 | 0·62 | 0·06 | 0·19 |
| | | Seeds | 2·57 | 0·57 | 2·40 | 0·49 | 0·54 | 0·07 | 0·12 |
| | | Sunflower | 2·50 | 0·57 | 2·25 | 0·62 | 0·55 | 0·06 | 0·16 |
| | | Corn | 2·00 | 0·48 | 3·50 | 1·18 | 0·64 | 0·07 | 0·20 |
| | | Soya | 2·28 | 0·51 | 2·61 | 0·57 | 0·59 | 0·08 | 0·15 |
| | | Olive | 2·07 | 0·74 | 2·44 | 0·43 | 1·01 | 0·09 | 0·17 |

[a] Unrefined oils.

FAAS, EAAS = flame or electrothermal atomic absorption spectrometry.

ours, perhaps due to the nature of the raw starting materials. However, most researchers (Fedelli *et al.*, 1973; Schütze and Müller, 1978; Tsai *et al.*, 1978; Rabascall *et al.*, 1985) have reported similar levels to those presented in this paper. Black (1975) has analysed several metals in samples of mill soybean oils from three locations in the USA, comparing three analytical methods for determining metals in oils. Our values were clearly lower for Fe and Zn, although Cu was of the same order of magnitude. Fe and Cu of some Spanish unrefined oils have shown levels much higher than ours. Our mean concentrations for Na are the highest

**Table 5. Most significant correlations ($p$ < 0·0001) for all samples and for each oil type**

| Type of oil | Equation[a] | C.C.[b] | N[c] |
|---|---|---|---|
| Total | $\lvert K\rvert = 0{\cdot}40\,\lvert Na\rvert - 0{\cdot}34$ | 0·77 | 109 |
| | $\lvert Ca\rvert = 3{\cdot}66\log\lvert Mg\rvert + 0{\cdot}52$ | 0·70 | 109 |
| | $1/\lvert Mg\rvert = 0{\cdot}55\; 1/\lvert K\rvert + 1{\cdot}51$ | 0·69 | 109 |
| | $\log\lvert Mg\rvert = 1{\cdot}05\log\lvert Na\rvert - 0{\cdot}81$ | 0·63 | 109 |
| | $1/\lvert Fe\rvert = 0{\cdot}05\; 1/\lvert Cu\rvert + 0{\cdot}31$ | 0·62 | 109 |
| | $1/\lvert K\rvert = 0{\cdot}20\; 1/\lvert Cu\rvert + 0{\cdot}31$ | 0·60 | 109 |
| | $\lvert Fe\rvert = 0{\cdot}97\, A + 0{\cdot}42$ | 0·55 | 109 |
| | $A = 0{\cdot}03\, P + 0{\cdot}04$ | 0·54 | 109 |
| Rapeseed | $\lvert Fe\rvert = 6{\cdot}42\,\lvert Cu\rvert + 0{\cdot}23$ | 0·83 | 20 |
| | $\lvert K\rvert = 0{\cdot}38\,\lvert Na\rvert - 0{\cdot}34$ | 0·84 | 20 |
| | $\lvert Ca\rvert = 5{\cdot}08\log\lvert Mg\rvert + 5{\cdot}39$ | 0·91 | 20 |
| Seed | $\lvert K\rvert = 0{\cdot}31\,\lvert Na\rvert - 0{\cdot}22$ | 0·74 | 20 |
| | $\lvert Mg\rvert = 0{\cdot}16\,\lvert Ca\rvert + 0{\cdot}09$ | 0·74 | 20 |
| | $\lvert Ca\rvert = 3{\cdot}75\log\lvert Mg\rvert + 4{\cdot}01$ | 0·71 | 20 |
| | $1/\lvert K\rvert = 1{\cdot}32\; 1/\lvert Mg\rvert + 0{\cdot}21$ | 0·83 | 20 |
| | $1/\lvert Mg\rvert = 0{\cdot}15\; 1/\lvert Cu\rvert + 0{\cdot}21$ | 0·83 | 20 |
| | $1/\lvert K\rvert\rvert = 0{\cdot}22\; 1/\lvert Cu\rvert - 0{\cdot}62$ | 0·82 | 20 |
| Sunflower | $\lvert Fe\rvert = 3{\cdot}85\,\lvert Zn\rvert - 0{\cdot}06$ | 0·82 | 18 |
| | $A = 1{\cdot}13\log\lvert Mg\rvert + 1{\cdot}00$ | 0·85 | 18 |
| | $\lvert K\rvert = 1{\cdot}81\,\lvert Na\rvert + 1{\cdot}46$ | 0·83 | 18 |
| | $\lvert Na\rvert = 1{\cdot}21\,\lvert Mg\rvert + 1{\cdot}75$ | 0·91 | 18 |
| | $\lvert Mg\rvert = 0{\cdot}63\,\lvert Ca\rvert - 0{\cdot}81$ | 0·88 | 18 |
| | $\lvert Ca\rvert = 2{\cdot}87\log\lvert Mg\rvert + 3{\cdot}86$ | 0·85 | 18 |
| | $\lvert K\rvert = 1{\cdot}24\log\lvert Mg\rvert + 1{\cdot}27$ | 0·83 | 18 |
| Corn | $\lvert K\rvert = 0{\cdot}39\,\lvert Na\rvert - 0{\cdot}31$ | 0·75 | 21 |
| | $1/\lvert K\rvert = 0{\cdot}31\; 1/\lvert Cu\rvert - 0{\cdot}21$ | 0·77 | 21 |
| | $1/\lvert Ca\rvert = 0{\cdot}96\; 1/\lvert Mg\rvert + 0{\cdot}22$ | 0·72 | 21 |
| | $\lvert Ca\rvert = 5{\cdot}43\log\lvert Mg\rvert + 6{\cdot}30$ | 0·68 | 21 |
| Olive | $\lvert K\rvert = 0{\cdot}97\,\lvert Na\rvert + 1{\cdot}48$ | 0·79 | 21 |
| | $1/A = 33{\cdot}3\,(1/P) - 0{\cdot}94$ | 0·83 | 22 |
| Soya | $\lvert K\rvert = 1{\cdot}84\,\lvert Na\rvert + 1{\cdot}35$ | 0·99 | 8 |

[a] In all cases, the concentrations values are in μg/g.
[b] C.C. = correlation coefficients.
[c] N = number of samples.

of those shown in Table 4, including those of mill olive (Solinas *et al.*, 1985) and soybean (Black, 1975) oils. However, K concentrations are similar to other published data from Italy for different commercial oils (Fedelli *et al.*, 1973; Solinas *et al.*, 1985) but much lower than those reported for mill oils (Black, 1975; Solinas *et al.*, 1985). This could be due to processing of crude oils (mainly filtration) that produces decreases of K and Ca concentrations whereas concentrations of Na do not change (Solinas *et al.*, 1985). Moreover, the ratio Na/K was always ≥1, which indicates, according to Prevot (1966), that the oils have undergone a refinement process. Concentrations of the alkaline-earth metals (Ca and Mg) are sensitively lower and slightly higher than mill soybean oil (Black, 1975) and a different commercial oil (Fedelli *et al.*, 1973), respectively.

The two parameters relating to quality indices (acidity and peroxide value), show low quality of the studied oils and this is noteworthy, as revealed by the high number of samples that surpass the maximum legislated for these parameters (B.O.E., 1983). Thus, 17% (18 samples) and 21% (23 samples) surpassed these maximum values for acidity and peroxides, respectively. Similar results have been observed by Rabascall *et al.* (1985) in two olive oil-producing areas of Catalonia, which were attributed to the poor quality of the olives. For both quality indices, the mean values found in the different types of studied oil can be arranged according to the following sequence:

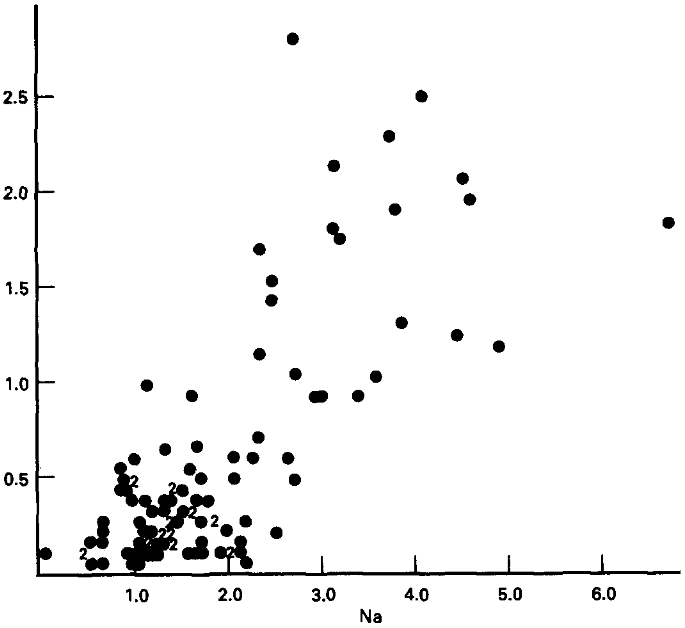

Fig. 1. Correlation between the concentrations of Na and K overall among analysed samples.

$$\text{olive} > \text{sunflower} > \text{corn} > \text{seeds}^{\dagger} > \begin{cases} \xrightarrow{A} \text{rapeseed} > \text{soya} \\ \xrightarrow{P} \text{soya} > \text{rapeseed} \end{cases}$$

$$\underbrace{\hphantom{\text{olive} > \text{sunflower} > \text{corn} > \text{seeds}^{\dagger} >}}_{A \text{ and } P}$$

where $A$ = acidity value and $P$ = peroxide value.

The poorest quality was found in the olive oils, presenting 54% and 33% of sample values above the legislated maximum.

Also, a correlation study was carried out between the concentrations of the metals studied and the quality indices, considering the samples overall and differentiating each type of oil. Direct, inverse and logarithmic variables of the studied parameters were considered in the statistical study of correlation. Table 5 shows the most significant correlations ($p$ < 0·0001) for the samples overall and for each type of oil. All the correlations were positive and the sunflower seed oil shows the greatest number of significant correlations. Among the correlations that have been found, the most important of all is that which exists between Na and K, which is repeated overall and within each type of oil. The rapeseed, seed and corn oils behave in a similar way, having very similar gradients and intercepts. Olive, sunflower and soya oils show greater gradients than the latter ones, and their intercepts are very similar. These differences in the mathematical equations for the different

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† Following the Spanish directorate, a mixture of rapeseed and another seed oil.

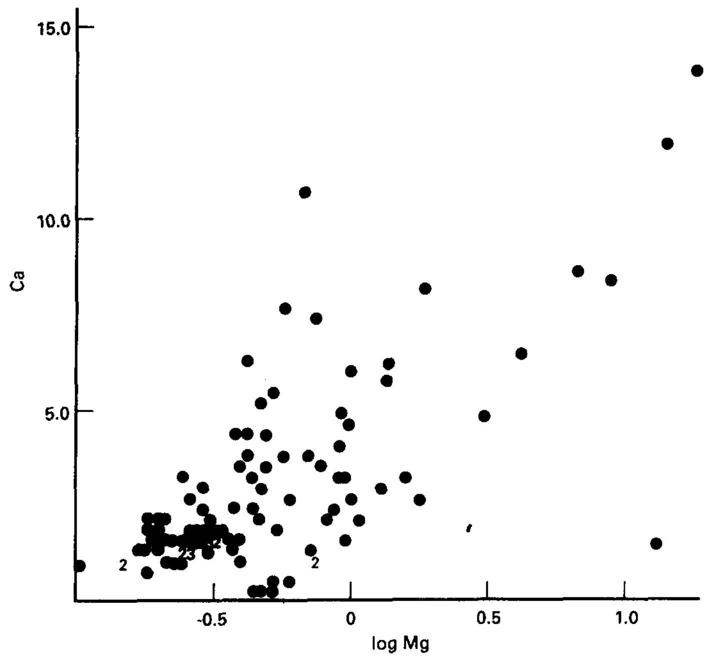

**Fig. 2.** Semilogarithmic correlation between Ca and log Mg overall among analysed samples.

oils may have originated from the different compositions of the raw starting materials. Figure 1 shows the correlation between the concentrations of Na and K in the total of the oil samples analysed. Direct correlations are observed between Ca and Mg and in four types of oil. The semilogarithmic correlation (Ca—log Mg), (Fig. 2) shows better correlation coefficients than the direct correlations. Both the gradients and the intercepts may be arranged according to the sequence corn > rapeseed > seed > sunflower, which could be attributed, as in the case described earlier, to differences in the raw starting material.

Among the remaining correlations, the most remarkable is the one that exists between the inverses of the concentrations of Fe and Cu, which is significant overall among the samples. A moderate correlation coefficient has been obtained between the acidity and the concentration of Fe overall among samples, which could be explained by the catalytic effects of Fe and other metals in the auto-oxidation of vegetable oils (Fedelli *et al.* 1973). Also, a positive correlation has been observed between acidity and peroxide values, probably because both parameters are related to the phenomenon of rancidity.

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