Catalytic Effect of Solid Metals on Thermal Stability of Olive Oils

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ABSTRACT: The influence of a series of metals—iron, copper, tin, and lead—on the thermal stability of olive oils of different origins and refined grades has been studied by applying thermal analysis techniques: thermogravimetry (TG) and derivative thermogravimetry (DTG). From thermogravimetric data it is deduced that iron and tin have a greater influence on oil oxidation, since the degradation rate increases. In the presence of copper and lead, important changes in the degradation rate are not observed, compared with the degradation in the absence of metals. The kinetic parameters, activation energy, and frequency factor of the oil degradation reaction were also calculated. The results obtained for both parameters confirm the negative influence of iron and tin on the oil oxidation process, regardless of the kind of oil tested.

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KEY WORDS: Activation energy, degradation rate, frequency factor, metals influence, olive oil, oxidation process, thermal stability, thermal analysis techniques.

Edible vegetable oils and, above all, olive oil, are relatively resistant to oxidation (autooxidation) because of their low proportion of polyunsaturated fatty acids and, more importantly, the antioxidants they have (1,2). However, once the oxidation process begins, it progresses quickly since it is an autocatalytic reaction. Moreover, the oxidation process, extensively studied from different points of view (3–7), can be influenced by internal or external factors, such as composition, temperature, light, and presence of metals.

In particular, the metals detract from the oxidative stability of the oil because they are powerful catalysts of its degradation, increasing the rate at which free radicals are generated (8). These are obtained by direct reaction of metal with the oil:

$$RH + M^{(n+1)+} \rightarrow R\bullet + H^+ + M^{n+} \quad [1]$$

or by hydroperoxide decomposition, arising from autooxidation of the oil:

$$ROOH + M^{(n+1)+} \rightarrow ROO\bullet + H^+ + M^{n+} \quad [2]$$

$$ROOH + M^{n+} \rightarrow RO\bullet + OH^- + M^{(n+1)+} \quad [3]$$

or also from the secondary oxidation products, such as alcohols or aldehydes (obtained from peroxides and hydroperoxides):

$$RCH_2OH + M^{(n+1)+} \rightarrow RCH_2O\bullet + M^{n+} + H^+ \quad [4]$$

$$RCH_2O\bullet + M^{(n+1)+} \rightarrow RCHO + M^{n+} + H^+ \quad [5]$$

Afterward, the secondary alcohols produce ketones and the aldehydes are further oxidized to the corresponding carboxylic acids. The formation of all these products causes loss of oil quality by producing alterations not only in the physicochemical properties but also in the organoleptic qualities of the oil.

Although there are studies in the literature that consider the influence of metals on edible vegetable oil oxidative stability (9–15), thermal analysis techniques have not been used in order to follow the degradative process. Such techniques allow one to study in a single way and by only one test the influences of temperature and the presence of metals on the oil degradation process.

This work presents a study of the influence of some metals (Cu, Sn, Pb, and Fe) on the thermal stability of olive oil in the heterogeneous phase by applying the following thermal analysis techniques: thermogravimetry (TG) and derivative thermogravimetry (DTG) under air atmosphere and isothermal conditions. Likewise, the thermodegradation reaction kinetic parameters, activation energy (E) and frequency factor (A), have been calculated from thermogravimetric data by applying the Arrhenius equation.

EXPERIMENTAL PROCEDURES

Apparatus and materials. All measurements were carried out on a Mettler Thermoanalyzer (model Thermoanalyzer-2; Mettler Instruments, Greifensee-Zürich, Switzerland) which is able to perform simultaneously the thermogravimetric (TG and DTG) and differential thermal analyses (DTA), with a temperature program between 25 and 1,000°C. It also can op-

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erate under a controlled gaseous atmosphere. The tested oil samples were introduced into alumina pans (10 × 4.5 mm in diameter). The tested metals were copper, lead, iron, and tin in metallic sheet form (2.5 × 0.24 cm, approximately).

Samples for testing. A Reagent Analysis (R.A.)-quality olive oil (**A**) and two commercial olive oils, a crude one (**B**) and a refined one (**C**), whose acidity indexes were 0.58 and 0.4%, respectively, have been used.

TG analysis and DTG analysis. About 20 µL of oil sample, previously degassed, were placed in the alumina pan and weighed on an analytical balance. Afterward, the metallic sheet was introduced as a reversed "U," in such a manner that the contact surface with the oil was the same for every case (50 mm^2, approximately). The pan was then introduced into the thermobalance, and thermograms were recorded under air atmosphere (100 mL · min^{-1}). A heating rate of 100°C · min^{-1} up to the temperature suitable for the isothermal heating was used. The tested temperatures were between 225–325°C. The study was started by carrying out an oil degradation test in the alumina pan in the absence of metal.

Kinetic study. From thermogravimetric curves, the necessary temperature and rate data for the calculation of the kinetic parameters, *E* and *A*, were extracted. To this purpose, the Arrhenius equation has been applied:

$$\log k = \log (dw/dt) = -(E/2.3RT) + \log A \qquad [6]$$

where *k* is the rate-specific constant, (*dw/dt*) is the degradation reaction rate, *E* is the activation energy, *R* is the gas constant, *T* is the absolute temperature, and *A* is the frequency factor.

The plots of log (*dw/dt*), for each tested temperature vs. the reciprocal of temperature (1/*T*, *K*) gave a straight line from which the *E* and *A* were obtained. The straight lines have been fitted by the least squares method, and from those the corresponding equations of the regression lines were obtained. For each case, the log (*dw/dt*) vs. (1/*T*) data points were determined from at least three replicate measurements.

RESULTS AND DISCUSSION

Thermogravimetric study. Figure 1 shows, as an example, the thermogravimetric curves (TG and DTG) of degradation of oil A under isothermal conditions in the absence of metal. In the figure the residual mass percentage (%w_r) for each tested temperature is plotted and the degradation rate (*dw*/*dt*, mg/min), obtained from the TG curve slope vs. time (min), TG and DTG curves, respectively.

Every curve shows similar shapes. It is observed in the curves that initially there is no change of mass, and the degradation rate is therefore zero. Afterward, the degradation rate increases, with greater increase in degradation rate at higher temperature. Finally, the rate is approximately constant and its value is greater at higher temperatures; this value is obtained at degradation percentages lower than 5% for every test.

The results obtained for each oil are summarized in Table 1. This Table shows the constant degradation rate values

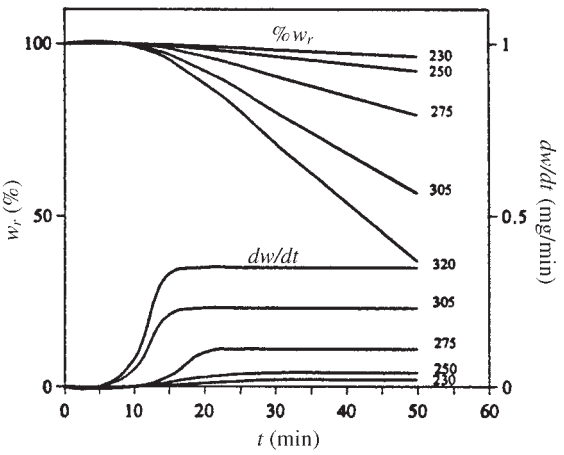

FIG. 1. Isothermal degradation of A (R.A. quality olive oil) in the absence of metal; *dw/dt*, degradation reaction rate. w_r, residual mass.

(third step of the DTG curve) obtained for each tested temperature, in the presence and absence of metals. It can be observed that the degradation rate is always larger at higher temperature. Likewise, the rate increases in the presence of iron or tin relative to the degradation in the absence of metals; however, in the presence of copper or lead, the degradation rates are similar to those obtained in the absence of metal for the three tested oils.

TABLE 1
Thermogravimetric Data of the Oil Degradation in the Absence and the Presence of Metals[a]

	Temperature (°C)			(*dw/dt*) · 10^2 (mg/min)[b]		
Metal	A	B	C	A	B	C
Alumina	230	230	235	2.0	1.5	1.0
	250	255	265	4.1	3.0	2.5
	275	280	280	11.0	9.0	6.0
	305	310	310	23.0	20.0	17.0
	320	330	330	35.0	37.5	30.0
Copper	225	225	230	1.0	1.5	0.6
	245	245	250	1.5	3.0	1.3
	275	270	280	5.0	4.0	3.5
	300	300	300	12.0	9.4	7.0
	335	335	320	33.0	31.3	20.0
Lead	225	220	225	1.5	1.2	0.7
	245	245	245	2.5	2.5	1.9
	265	275	270	4.5	6.0	2.8
	295	305	300	15.0	16.5	10.0
	320	330	335	31.5	35.0	30.0
Iron	220	220	220	6.0	4.0	4.0
	240	240	240	10.0	7.5	8.0
	265	270	265	17.0	15.0	14.0
	290	295	290	34.0	25.0	27.5
	315	335	315	57.0	40.0	40.0
Tin	220	230	230	3.0	3.5	2.3
	245	250	250	5.0	7.0	4.3
	270	275	275	12.5	11.0	11.0
	290	300	300	20.0	23.0	16.0
	320	325	325	39.6	40.0	30.0

[a]indicated as alumina. Absence
[b]Degradation rate. (A) R.A. quality olive oil; (B) crude olive oil; (C) refined olive oil.

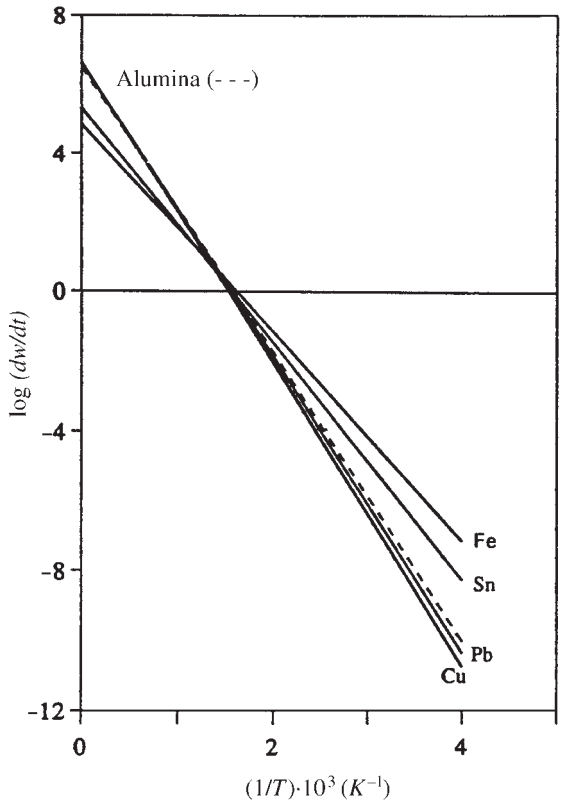

FIG. 2. Regression line of A (R.A. quality olive oil) degradation in the presence of metals. *T*, absolute temperature; *dw/dt*, rate of degradation.

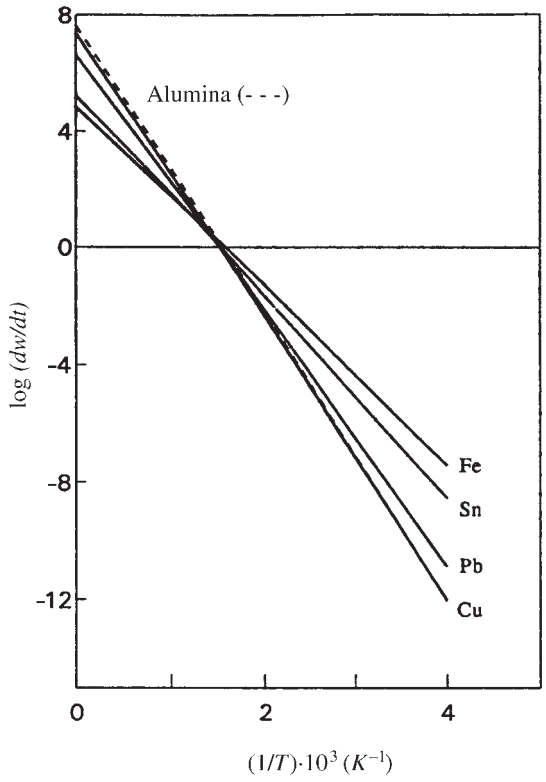

FIG. 3. Regression line of B (crude olive oil) degradation in the presence of metals; see Figures 1 and 2 for abbreviations.

Kinetic study. To carry out the kinetic study of the thermodegradation reaction, in the absence or presence of metals, the constant degradation rate values obtained for each temperature (summarized in Table 1) have been used.

The plots of log (*dw*/*dt*) vs. (1/*T*) give a straight line from whose slope (–*E*/2.3*R*) and intercept with the *y* axis (log *A*) the *E* and *A* are calculated, respectively. In Figures 2–4 the straight lines obtained for the oils A, B, and C are represented in the absence (indicated as alumina) and presence of metals.

Table 2 indicates the regression line equations for each case, and the kinetic parameters obtained from them (activation energy and frequency factor). In this table, the correlation coefficient (*R*) and deviation coefficients of the slope [*S*(*a*)] and origin [*S*(*b*)] obtained for each line, which show the level of uncertainly in the measurements, also are indicated.

The results summarized in Table 2 show that the activation energy and frequency factor obtained in the absence of metal are similar to that obtained in the presence of copper. When iron or tin is present, the values are lower for the tested oils. Thus, the activation energy obtained for oil A in the absence of metal is 79 ± 3 kJ/mol, which decreases to 57 ± 2 kJ/mol in the presence of iron and 65 ± 4 kJ/mol in the presence of tin. For oil B, the values obtained are 50 ± 3 and 63 ± 3 kJ/mol in the presence of iron and tin, respectively, against 80 ± 5 kJ/mol obtained in the absence of metal. Finally, for oil C, the activation energy decreases from 94 ± 5 kJ/mol, corresponding to the

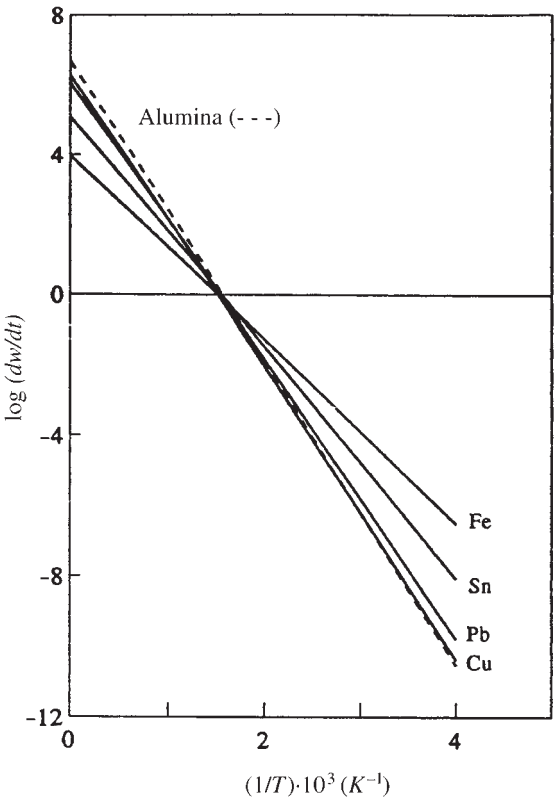

FIG. 4. Regression line of C (refined olive oil) degradation in the presence of metals; see Figures 1 and 2 for abbreviations.

TABLE 2
Kinetic Values of Oil Degradation in the Absence and the Presence of Metals[a]

Metal	Oil[b]	Straight-line equation	*R*	*S(a)*	*S(b)*	Activation energy (kJ/mol)	Frequency factor (cm^3/mol·s)
Alumina	A	$y = -4.1223x + 6.5082$	0.998	0.135	0.248	79 ± 3	$3.22 \cdot 10^6$
	B	$y = -4.3100x + 6.7097$	0.997	0.194	0.352	82 ± 4	$5.13 \cdot 10^6$
	C	$y = -4.9176x + 7.6375$	0.995	0.277	0.500	94 ± 5	$9.18 \cdot 10^7$
Copper	A	$y = -4.3325x + 6.6258$	0.996	0.235	0.431	83 ± 5	$4.23 \cdot 10^6$
	B	$y = -4.1721x + 6.3008$	0.994	0.256	0.471	80 ± 5	$2.00 \cdot 10^6$
	C	$y = -4.8483x + 7.3791$	0.993	0.341	0.624	93 ± 7	$2.39 \cdot 10^7$
Lead	A	$y = -4.2272x + 6.5956$	0.994	0.273	0.506	81 ± 5	$3.94 \cdot 10^6$
	B	$y = -3.9709x + 6.0872$	0.997	0.183	0.336	76 ± 3	$1.22 \cdot 10^6$
	C	$y = -4.3792x + 6.6410$	0.992	0.326	0.600	84 ± 6	$4.38 \cdot 10^6$
Iron	A	$y = -2.9934x + 4.8348$	0.999	0.091	0.169	57 ± 2	$6.84 \cdot 10^4$
	B	$y = -2.6232x + 3.9703$	0.993	0.180	0.333	50 ± 3	$9.34 \cdot 10^3$
	C	$y = -3.0630x + 4.8438$	0.997	0.440	0.263	59 ± 3	$6.98 \cdot 10^4$
Tin	A	$y = -3.3835x + 5.3026$	0.996	0.185	0.344	65 ± 4	$2.01 \cdot 10^5$
	B	$y = -3.2913x + 4.8438$	0.997	0.152	0.278	63 ± 3	$1.25 \cdot 10^5$
	C	$y = -3.5128x + 5.3666$	0.994	0.219	0.402	67 ± 4	$2.33 \cdot 10^5$

[a]Absence of metal indicated as "alumina."
[b]See Table 1 for abbreviations.

process in the absence of metal, to 59 ± 3 and 67 ± 4 kJ/mol in the presence of iron and tin, respectively. Likewise, for the three tested oils, a remarkable decrease of frequency factor occurs in the presence of those metals (iron and tin). On the other hand, when lead is present in oil B or C, the decrease of the activation energy and of the frequency factor is little, while for oil A a decrease is not observed. These results could be explained because iron, tin, and lead are more active (they are above hydrogen in the table of standard reduction potentials), and the free acidity of the oil would favor the dissolution of those metals; with the copper it is not possible and therefore would explain its lower activity.

In conclusion, the application of isothermal TG allows one to study quickly the catalytic effect of metals on the thermal stability of vegetable oils. The presence of iron or tin produces a noticeable increase in reaction rate relative to the degradation in the absence of metal, while copper and lead give rate values similar to those obtained in the absence of metal.

The activation energies of the degradation reaction in the presence of iron and tin are much lower than those obtained in the absence of metal. These decreases are about 30% for iron and about 25% for tin. The values for copper and lead are similar to those obtained in the absence of metal. These results confirm the negative influence of metals, as iron or tin, on the thermal stability of vegetable oils.

Independent of the metal type, it can be observed that the activation energy and frequency factor values are higher for oil C than those for oil A or B, which confirms that the thermal stability of oil C is greater.

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