Determination of Trace Elements in Edible Vegetable Oils by Atomic Absorption Spectrophotometry

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Methods are described for the direct determination of Al, Cr, Cu, Fe, Ni and Pb by atomic absorption spectrophotometry in sunflower oil and olive oils. Metallic contamination after storage under different controlled conditions and in contact with carbon steel, austenitic steel, ferritic steel and aluminum was examined. Additionally, chemical characteristics related to quality (acid value, peroxide value, K_{270} and oxidative stability) and some physical parameters of interest were evaluated after storage. When the samples were atomized directly off the tube wall, matrix interferences were not observed in the determination of Cr, Cu, Ni and Pb, whereas such interferences were noted when Al and Fe were determined. The results indicated that the L'Vov platform for Al and Fe determinations eliminates the matrix effects. Contamination with Fe was only detected in the olive oil that had been in contact with carbon steel, Fe concentration increased from 120 ± 12 to 3,520 ± 157 ppb. The physicochemical characteristics were affected only by the storage conditions, regardless of the metal sheets with which they were in contact. Virgin olive oil showed lowered stability after storage in contact with a carbon-steel sheet than when stored in absence of metal.

KEY WORDS: Atomic absorption spectroscopy, graphite furnace, trace metals, vegetable oils.

Edible fats and oils are frequently subjected to processing, including refining, bleaching and deodorization (1,2), which inevitably makes the oils come in contact with metallic surface areas, often at high temperatures. Many reports have described the deleterious effects that trace metal contamination, particularly iron and copper (3–5), have on the flavor and oxidative stability of oils.

At present, determination of trace elements in oils is based on the direct aspiration of the samples, diluted in a suitable organic solvent (i.e., methyl-isobutylketone), into an air-acetylene flame. Although simple and rapid, it suffers from loss of sensitivity. Methods requiring a pretreatment of the samples to destroy the organic matrix involve certain manipulations and the subsequent risk of sample contamination on analyte loss (6–11).

We report here rapid analytical methods for the determination of trace metals in oils and have applied them to the analysis of metallic contamination in several commercial oils. Physical and chemical changes relating to oil quality are reported.

EXPERIMENTAL PROCEDURES

Samples. The oils used in this study were purchased locally: extra virgin olive oil; virgin olive oil; olive oil (a blend of virgin and refined olive oil); refined olive oil (12); and refined sunflower oil. One sheet (8 × 8 cm^2) of either carbon steel, austenitic steel (18% Cr, 8% Ni) ferritic steel (16% Cr) or aluminum was introduced into two liters of oil. A fifth sample of oil was devoid of metallic contact and served as a control. Samples were stored at 40°C and analyzed after 10, 20 and 30 d.

Physicochemical parameters. Density (13), refractive index (14), acid value (AV) (15), peroxide value (PV) (16), absorptivity at 270 nm (K_{270}) (17), moisture (18) and insoluble impurities (19) were determined according to International Union of Pure and Applied Chemists standard methods. Stability was determined by the Rancimat method (Metrohm 679, Herisau, Switzerland) (20), and conductivity was measured with a temperature-controlled conductimeter. (Crison 525, Barcelona, Spain).

Analysis of metal contents. Trace metal content was determined on a Perkin-Elmer 3030 (Norwalk, CT) atomic absorption spectrophotometer, equipped with a graphite furnace (Perkin-Elmer HGA-400) and an automatic sample injector (Perkin-Elmer AS-40). Both the standard curve (21,22) and the standard addition (23–25) methods were used. Organo-metallic standards of Al, Cr, Cu, Fe, Ni and Pb were used at concentrations of 5000 ppm in an oily matrix (Conostan, Ponca City, OK). A vegetable oil of low metal content was obtained by dissolving a part of refined oil in 3 parts of hexane and then eluting with 5 parts of hexane through a column of aluminum oxide (Fluka, Buchs, Switzerland), which was previously activated by heating in a oven at 150°C for 14 h. Twice the recommended mass of aluminum oxide was used. Hexane of the eluate was eliminated by stripping under reduced pressure (21). Samples for the determination of Al, Cr, Cu, Fe and Ni were prepared as follows: A solution of oil in methyl-isobutylketone (MIBK), within the linear range of 0.2–0.6 absorbance units (peak area), was prepared by weighing 0.5–2.5 g of previously filtered oil and making up the volume to 10 mL with MIBK (26). For Pb determination, MIBK was diluted with a 2% solution of egg lecithin (Merck, Darmstadt, Germany), which acted as a matrix modifier (22). The spectrophotometric conditions and temperature programs for the graphite furnace, corresponding to each element, were as prescribed in the Standard Perkin-Elmer cookbook. For Al, Cr, Fe and Ni determinations, pyrolyzed tubes with a L'Vov platform were used.

Statistical methods. The confidence limits (L_C), detection limits (L_D) and quantitation limits (L_Q) were determined as described by Currie (27) by following the methodology of Vioque and Albi (28). Table 1 shows these limits for each metal as calculated from three subsamples and three replicates. Metal content measurements were determined from means values of the three replicates, and the coefficient for all samples variation was less than 5%.

TABLE 1

Confidence Limits (L_C), Detection Limits (L_D) and Quantitation Limits (L_Q) (ppb by weight)

	Al	Cr	Cu	Fe	Ni	Pb
L_C	2.2	3.6	0.6	3.3	7.5	1.8
L_D	13.6	6.8	1.3	4.4	14.9	6.6
L_Q	41.4	10.8	3.8	13.4	45.4	20.1

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TABLE 2

Fe Determination in Extra Olive Oil: Atomization off the Wall (AW) and Atomization off the Platform (AP) (ppb by weight)

	Days at 40°C	No sheet	Carbon steel	Austenic steel	Ferritic steel	Aluminum
AW[a]	10	260	281	281	272	315
	20	278	287	283	277	263
	30	283	317	302	319	292
AW[b]	10	427	440	403	490	394
	20	470	508	524	412	454
	30	430	446	448	471	447
AW[c]	10	499	495	519	458	484
	20	486	516	497	479	481
	30	481	492	453	490	477
AP[d]	10	237	257	257	247	287
	20	253	261	257	252	239
	30	257	288	275	290	266
AP[e]	10	217	257	237	226	244
	20	217	237	257	252	239
	30	265	256	255	216	240

[a] Standard curve, dilution 1:10 (wt/vol), ±20 ppb.
[b] Standard addition, dilution 1:20 (wt/vol), ±40–140 ppb.
[c] Standards with low iron content oily matrix, dilution 1:10 (wt/vol), ±20 ppb.
[d] Standard curve, dilution 1:10 (wt/vol), ±35 ppb.
[e] Standard addition, dilution 1:10 (wt/vol), ±20–35 ppb.

RESULTS AND DISCUSSION

Selection of methods. Possible matrix interference effects produced by oil were studied. They occurred only when Fe or Al were being determined. For comparative purposes and to select the most adequate method, the iron contents of the fifteen extra-virgin olive oil samples were measured (a) by atomization off the wall while using (i) a standard curve obtained by dissolving the standard only in MIBK; (ii) the method of additions; and (iii) a standard curve obtained from a standard dissolved in a solution of iron-free oil in MIBK in the same proportions as in the samples to be determined; or (b) by atomization off the platform while using (i) a standard curve obtained with a standard dissolved only in MIBK and (ii) the method of additions. The results are shown in Table 2.

Similar values were obtained by all methods, except those resulting from the method of atomization off the wall (Table 2, footnotes b and c), which were generally higher. Interference produced by the matrix resulted in a drop in the absorbance value. Consequently, when a standard curve is plotted (from oil that contains standards) or when the method of addition is used, the line has a lower slope than that obtained from oil standard free. This fact explains the differences in iron content obtained from both standard curves and the method of additions (Table 2, footnotes a–c).

Use of the platform avoided dispersion of the sample inside the tube, improved reproducibility of measurements and led to a complete mineralization of samples with low thermal conductivity, such as oils, thus creating a more uniform temperature. The close agreement between the results shown in Table 2 (footnotes d and e) demonstrates the advantages of the platform in eliminating matrix interferences. It was also shown that when the tube was used without a platform, the final result was affected by the proportion of oil in the solution injected into the furnace. This fact is illustrated in Figure 1A, which shows the differences in the slopes of a standard curve obtained with standard solutions containing iron-free oil in a proportion of 1:10 (wt/vol), a second curve corresponding to determination by the method of addition from a sample

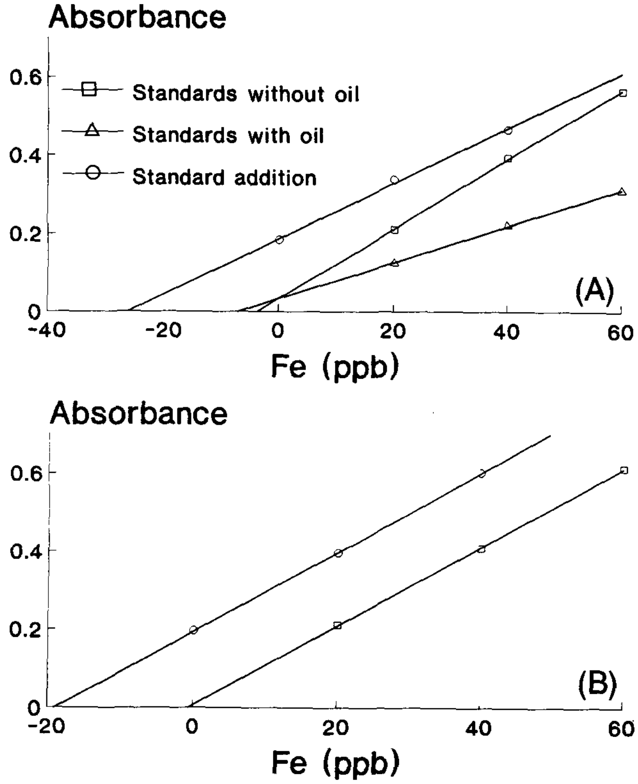

FIG. 1. Standard addition and calibration curves by (A) atomization off the wall (B) atomization off the platform.

diluted 1:20 (wt/vol) and a third curve obtained with oil-free standards. When the L'Vov platform was used, the calibration and standard addition curves had the same slope (Fig. 1B), which shows that the matrix effects have been minimized.

Accordingly, Fe was determined in the remaining oils by using the platform within the tube with standard solutions in MIBK. The same method was used to measure Al, Cr and Ni. When the Cu and Pb were determined, matrix interferences were not observed, and therefore, the platform was not used for these elements. For those samples with the highest Cu and Pb contents, the results obtained by standard curve and by the method of addition were similar.

Metal content of the treated oils. The Al, Cr, Cu, Fe, Ni and Pb contents of the 80 samples (75 treated oils and 5 original oils) were determined, and the results are shown in Table 3. No significant differences were observed in metal contents before and after treatment, except for virgin olive oil treated with carbon-steel sheet (Table 4). These results appear consistent with the initial acid values. Virgin olive oil showed the highest AV (2.40) compared to the other oils tested, which were lower than 0.63.

Physicochemical parameters. Figure 2 shows changes in PV, while Figure 3 shows K_{270} values, for oils subjected to the different treatments. Figure 4 illustrates the evaluation of oxidative stabilities. Density, refraction index, AV, moisture, insoluble impurities and conductivity did not change significantly.

Regardless of the type of metal used, the changes occurring in PV, K_{270} and oxidative stability values followed the same pattern and agreed with those expected in the oils tested after prolonged storage under adverse conditions (29–32).

The oxidative stability of the oils behaved similarly regardless of their treatment. An exception was virgin olive oil treated with carbon steel, which showed the greatest loss in stability after 30 d of treatment at 40°C. One month of storage showed an increased iron content, which may account for this result.

TABLE 3

Metal Contents (in ppb by weight)

	Extra[a] virgin	Virgin[a] olive	Olive[a]	Refined[a] olive	Sunflower[a]
Al	40-55 (±7)	33-42 (±3)	80-100 (±7)	46-64 (±7)	22-35 (±3)
Cr	$<L_D$	$<L_D$	$<L_D$	$<L_D$	$<L_D$
Cu	$<L_D$	73-86	$<L_D$	$<L_D$	$<L_D$
Fe[b]	237-290 (±35)	120-150 (±12)	1400-1730 (±173)	158-176 (±35)	182-203 (±35)
Ni	$<L_D$	$<L_D$	$<L_D$	$<L_D$	$<L_D$
Pb	$<L_D$	$<L_D$	11-15 (±3)	$<L_D$	$<L_D$

[a] Each pair of values corresponds to the minimum and the maximum of the pooled values obtained from sixteen samples of the oil indicated in each column (one sample of untreated oil plus fifteen samples of the treated oils). L_D = detection limit.

[b] The data corresponding to the iron contents do not include the results from samples treated with carbon steel.

TABLE 4

Effect of Storage on Iron Content of Oils Treated with Carbon Steel

Days at 40°C	Extra virgin	Virgin olive	Olive	Refined olive	Sunflower
10	257 (±35)	200 (±35)	1,400 (±173)	163 (±35)	185 (±35)
20	261 (±35)	344 (±35)	1,450 (±173)	176 (±35)	187 (±35)
30	288 (±35)	3,520 (±157)	1,677 (±173)	170 (±35)	188 (±35)

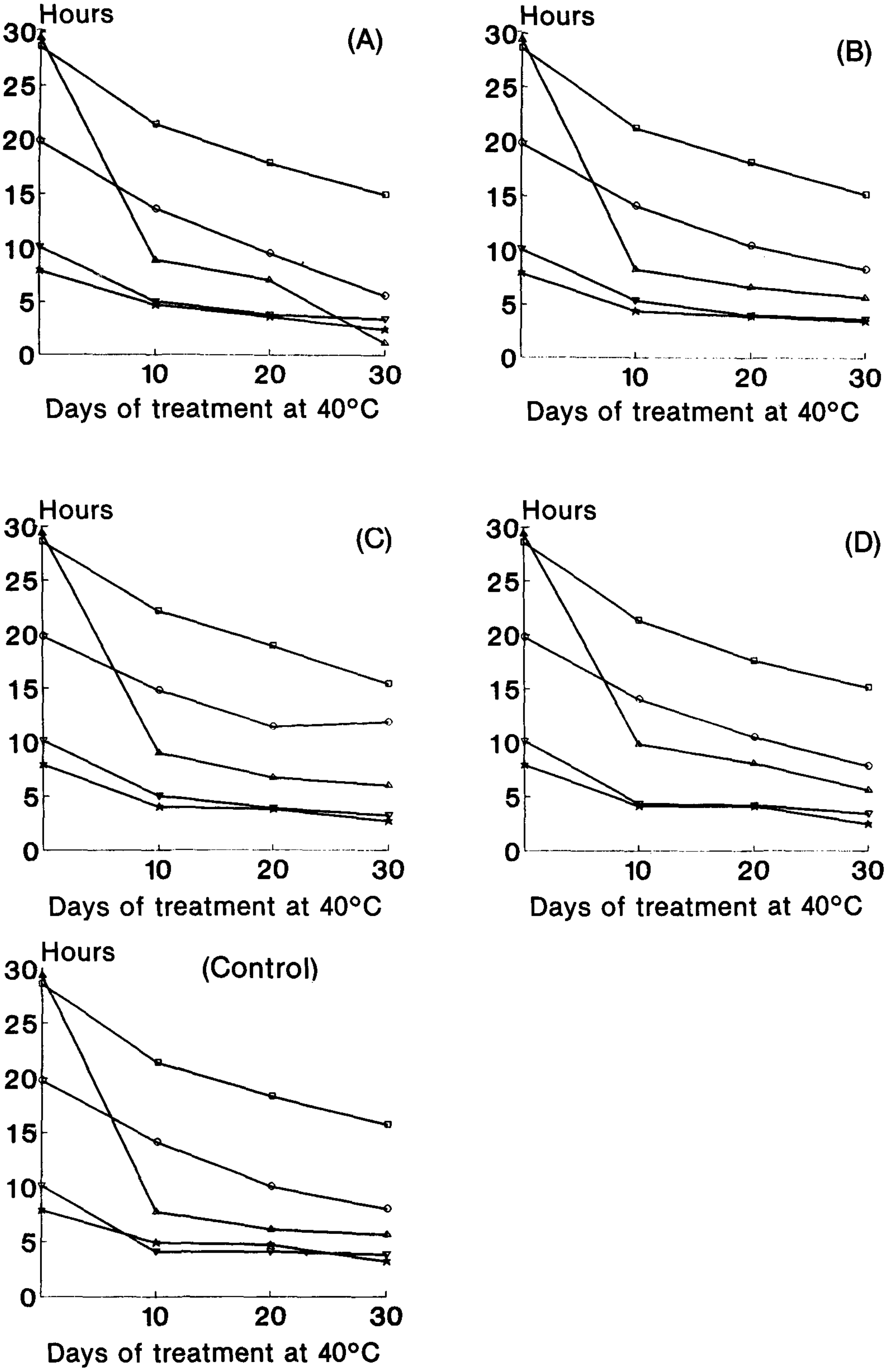

FIG. 2. Changes in peroxide value of treated oils (Control) without metal sheet, (A) carbon steel sheet, (B) austenitic steel sheet, (C) ferritic steel sheet and (D) aluminum. -⊟-, Extra virgin olive; -△-, virgin olive; -⊖-, olive; -▽-, refined olive; -✱-, sunflower.

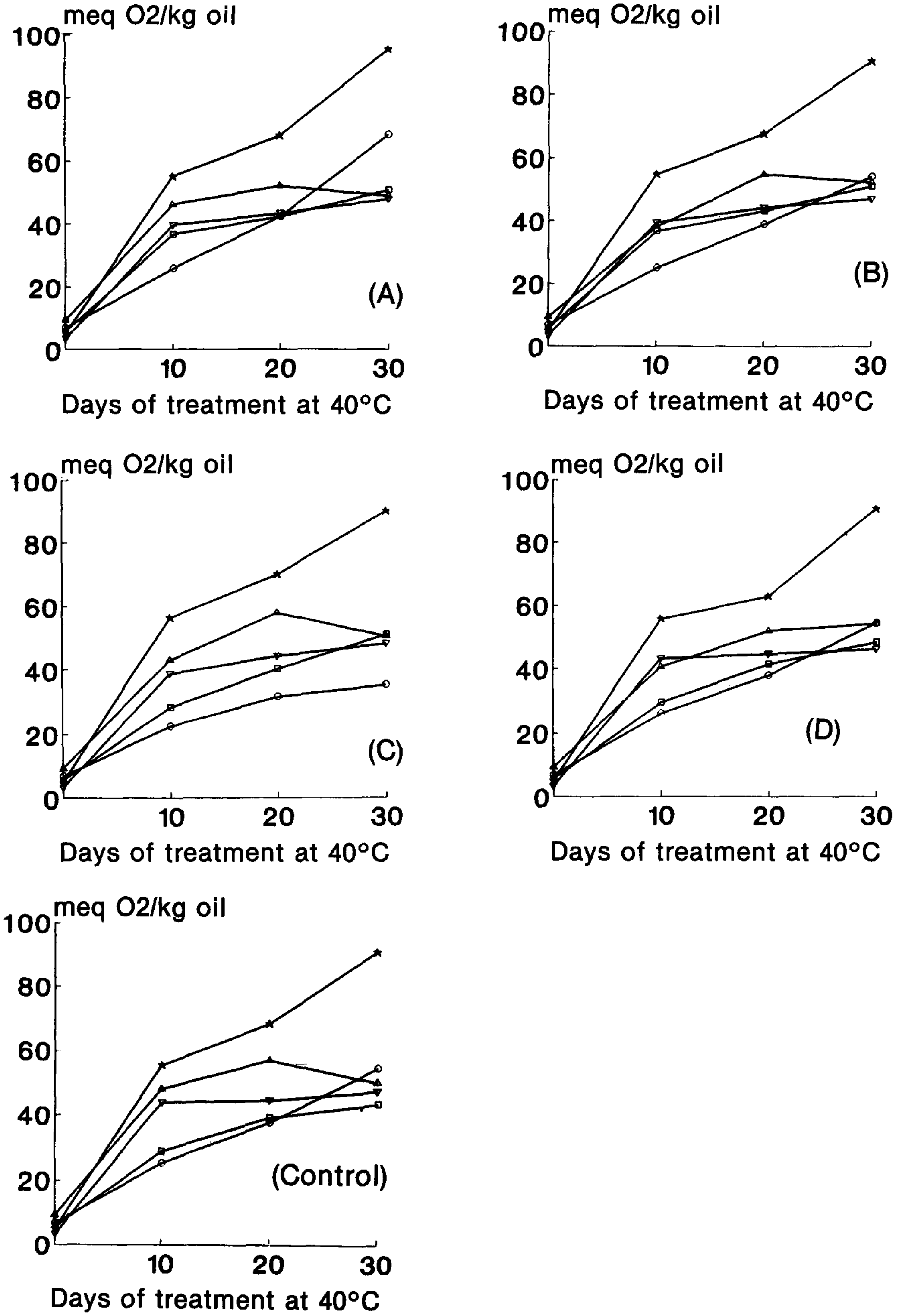

FIG. 3. Changes in K_{270} values (Control) without metal sheet, (A) carbon steel sheet, (B) austenitic steel sheet, (C) ferritic steel sheet and (D) aluminum. See Figure 2 for symbols.

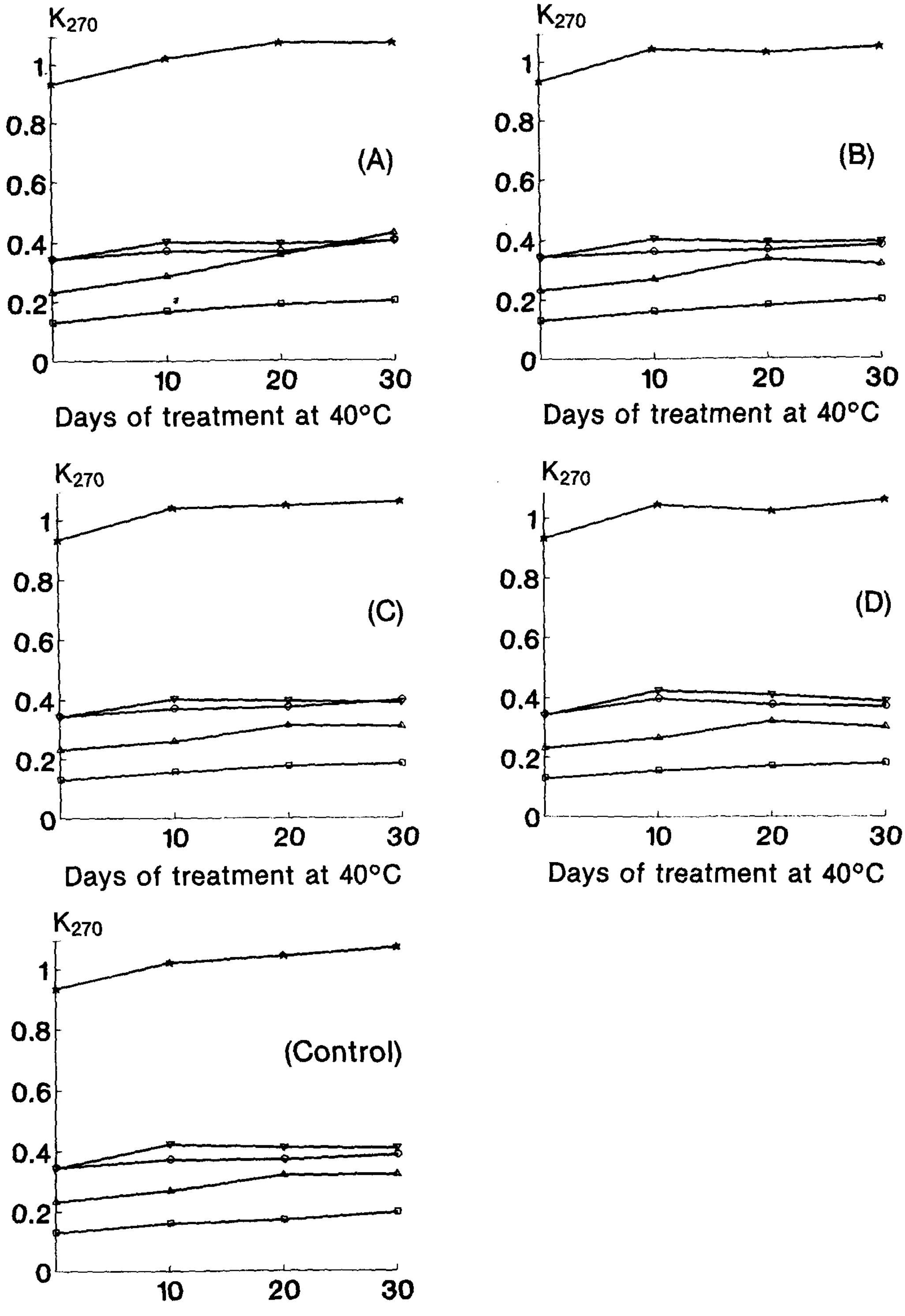

FIG. 4. Changes in oxidative stability (Control) without metal sheet. (A) carbon steel sheet, (B) austenitic steel sheet, (C) ferritic steel sheet and (D) aluminum. See Figure 2 for symbols.

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