

Determination and Levels of Chromium in French Wine and Grapes by Graphite Furnace Atomic Absorption Spectrometry

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An accurate and precise method for direct determination of chromium in wine using graphite furnace atomic absorption spectrometry (GFAAS) is described. The method was also applied to grape samples treated by previous acid mineralization. A total of 79 wine samples from different regions in France and 12 grape samples of different varieties were analyzed. Chromium levels ranged from 7.0 to 90.0 $\mu\text{g/L}$ in red wines, from 6.6 to 43.9 $\mu\text{g/L}$ in white wines, from 7.3 to 14.7 in rosé wines, and from 10.5 to 36.0 $\mu\text{g/L}$ in champagne. Deficient conditions in wine storage could increase chromium content. In grape samples, chromium content varied from 2.5 to 20.9 $\mu\text{g/kg}$ for white varieties and from 2.4 to 64.6 $\mu\text{g/kg}$ for red varieties. The contribution of wine consumption to total Cr daily dietary intake for the French population was estimated to be 4.06 μg per resident. The daily contribution of chromium from wine does not exceed 10% of dietary intake.

Keywords: Chromium; wine; dietary intake; GFAAS

INTRODUCTION

Chromium is a naturally occurring element in the environment and in most foodstuffs. Several studies have investigated the chemistry of Cr in soil and its uptake by plants (Ramachandran et al., 1980; Cary and Kubota, 1990). Soil contamination is an important factor contributing to total Cr concentration in plant tissues; samples taken from plants growing on high-Cr soils contained higher Cr concentrations than similar plants growing on low-Cr soils (Cary and Kubota, 1990). Anthropogenic sources also can increase Cr content in the environment and, subsequently, in the food chain (Hughes et al., 1994; Alvarez-Cabal et al., 1994). The main sources of Cr in the environment include industrial and urban sewage, waste chromates from electroplating baths, corrosion inhibitors from heat exchange systems, and trade effluents from tanning processes (Alvarez-Cabal et al., 1994; Soares et al., 1994). In addition, technology used in food and beverage processing can increase the Cr content in these products. The dissolution of Cr from stainless steel, widely used in the food industry, is probably the main source of Cr contamination of food and beverages (Reilly, 1980; Concon, 1988).

Chromium is one of the essential trace elements in the human body, as it appears to play a role in the metabolism of glucose and some lipids (mainly cholesterol) (Mertz, 1969; Anderson, 1981; Brichard et al., 1993; Hughes et al., 1994; Morris et al., 1995). However, adverse effects may occur at higher concentrations (Hughes et al., 1994). Excessive amounts of Cr, particularly in the more toxic Cr(VI) valence state, may be involved in the pathogenesis of some diseases such as lung and gastrointestinal cancers (Goyer, 1991; Alvarez-Cabal et al., 1994; Hugues et al., 1994).

Ingestion in food and beverages likely represents the principal route of chromium intake by humans. The estimated safe and required dietary intake of Cr is 0.05–0.20 mg/day (National Research Council, 1989). Wine could contribute an important fraction of total dietary intake of Cr (Darret et al., 1986; Minoia et al., 1994). Therefore, additional data on Cr content in wine and the possible role of wine consumption on total dietary Cr intake are required. Wine is a complex matrix containing a variety of mineral and organic substances in an ethanol–aqueous solution. The principal dissolved species are inorganic ions (ca. 2g/L) such as K^+ , Na^+ , and Ca^{2+} , organic acids such as tartaric, lactic, and citric acid, polyphenols such as anthocyanins and tannins, polyhydroxy alcohols such as glycerol (ca. 7g/L), and various proteins, amino acids and polysaccharides. Graphite furnace atomic absorption spectrometry (GFAAS) is currently used to determine Cr concentrations in food, beverages, and biological samples (Alvarez-Cabal et al., 1994; Minoia et al., 1994; Boughriet et al., 1994; Soares et al., 1994; Chevreuril et al., 1995; Vinas et al., 1995). Here we describe a rapid method for determination of chromium content in wine by GFAAS. We used this method to determine Cr levels in 79 wine samples from different regions of France (including red wine, white wine, rosé wine, and champagne) and grape samples of 12 different varieties treated with previous sample acid mineralization. We also evaluated the contribution of these Cr levels to daily dietary intake of this element for the French population.

MATERIALS AND METHODS

Apparatus. A Varian 1275 double-beam atomic absorption spectrophotometer equipped with a deuterium background corrector was used at a slit width of 0.2 nm, with a 4-mA hollow cathode lamp of Cr. The samples were atomized for Cr determinations at 357.9 nm under the conditions shown in Table 1. A Varian GTA-95 furnace and pyrolytic graphite tubes were used. The samples were injected automatically by a Varian autosampler. Nitrogen of 99.99% purity at 300 mL/min flow was used as the internal gas. Signals were recorded

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Table 1. Graphite Furnace Programs for the Determination of Chromium in Wine and Mineralized Grape Samples by GFAAS^a

step	temp, °C	time, s	gas flow, mL/min	read
injection	85	5	3.0	
dry ashing	95	60	3.0	
	120	10	3.0	
	300	8	3.0	
	500	10	3.0	
	800	10	3.0	
	1000	20	3.0	
	1000	1	0	
atomize	2600	0.8	0	*
	2600	1	0	*
clean	2600	2	3.0	

^a Wavelength, 357.9 nm; current lamp intensity, 4 mA; slit, 0.2 nm; background correction, deuterium lamp; measurement mode, peak height; gas, nitrogen.

in peak-height mode with an Epson RX-80 chart recorder. A microwave digestion system, Maxidigest MX 350 Prolabo, equipped with Pyrex digestion vessels, was used for grape sample mineralization, and an electric oven was used to mineralize wine samples.

Reagents. All solutions were prepared from deionized water obtained by bidistilling water immediately before use. A chromium standard solution of 1.00 ± 0.002 g/L (Merck) was used for calibration. Nitric acid (65%) (Merck, Suprapure) was used as a chemical modifier. Hydrochloric acid (37%) (Merck, Suprapure) was used for wine sample mineralization. For grape sample mineralization, nitric acid (65%) (Merck, Suprapure), hydrogen peroxide solution (35%) (Merck, reagent grade), and perchloric acid (70–72%) (Merck, Suprapure) were used.

Materials. To eliminate absorbance due to detergents and samples, all glassware and polyethylene containers were washed with bidistilled water after each use, decontaminated by vapor-cleaning with nitric acid, and rinsed several times with ultrapure water.

Samples. We analyzed 79 samples of different French wines in commercial bottles (red, white, rosé, and champagne wines). The wine samples analyzed were from different wine-growing regions and of different vintage years. All wines analyzed are frequently consumed in France. The same wine of 7 different vintage years (1980, 1983, 1988, 1989, 1990, 1991, and 1993) was also tested. In addition, grape samples of 12 different varieties were analyzed.

Procedure. *Wine Samples.* Chromium was directly determined by GFAAS in wine samples, but to detect possible matrix effects, a mineralization sample procedure was also tested. Dried mineralization treatment was applied to four wine samples. Portions of a 50.0-mL wine sample were placed in a quartz capsule and evaporated in a water bath at 130 °C to dry residue. The capsule containing dried sample was then placed in an electric oven, and white ashes were obtained in 180 min at 550 °C. The ashes were cooled, dissolved with 2 mL of HCl, and diluted to a total volume of 50.0 mL in a glass volumetric flask with bidistilled water.

Grape Samples. Prior to GFAAS analysis, 25 mL of HNO₃, 3 mL of H₂O₂, and 5 mL of HClO₄ were added to 20.0-g grape samples and the samples were submitted to a microwave digestion (power was 60% for 1 min, 30% for 10 min, 15% for 3 min, and 40% for 15 min). The solution was then diluted to a total volume of 50.0 mL in a glass volumetric flask with bidistilled water.

Sample Analysis. Chromium was determined directly by GFAAS in wine samples and in mineralized wine and grape samples. Champagne samples were previously degasified in an ultrasonic bath. The same procedure was followed for the blanks.

RESULTS AND DISCUSSION

Graphite Furnace Program. The furnace conditions (Table 1) were optimized on the basis of time–

Table 2. Chromium Concentrations (Micrograms per Liter) in Different Types of Wines

type of wine (<i>n</i>)	av	range
red (61)	22.6	7.0–90.0
white (11)	21.3	6.6–43.9
rosé (2)	11.0	7.3–14.7
champagne (6)	25.1	10.5–36.0

Table 3. Chromium Concentrations for Different Vintages of Wine from the Same Vineyard and Winery

vintage sample ^a	age of wine, years	chromium, µg/L
1980	13	19.7
1983	10	16.2
1988	5	12.7
1989	4	19.6
1990	3	13.5
1991	2	9.4
1993	0	8.0

correlation analysis^b
(age of wine vs Cr concentration)
regression $y = 0.750x + 10.19$ $r = 0.750^c$

^a Each sample corresponds to a sweet red wine produced via the same process each year. ^b r = coefficient of correlation. Threshold of significance at 2% = 0.748; at 5% = 0.666. ^c Highly significant correlation.

temperature studies. Mineralization of the matrix was complete after heating to 1000 °C for 20 s. The atomization temperature yielding maximum signals was 2600 °C. Stopping the flow at this point enhanced sensitivity without compromising the sensitivity or lifetime of the tube.

The method for direct Cr determination in wine samples was validated by comparison with Cr determinations in mineralized samples, using the same furnace conditions (Table 1). Results showed no significant difference between direct and mineralization procedures for all samples tested ($p \leq 0.05$, F test). Removing the mineralization procedure greatly simplified and reduced the cost of the analysis.

Calibration and Analytical Characteristics. The calibration plot was obtained using solutions ranging from 1.0 to 7.5 ng/mL prepared from a working solution of 10 ng/mL. The equation for the calibration plot was as follows: absorbance = $0.062 [\text{Cr, ng/mL}] + 0.017$, where $r = 0.9997$ and $\alpha = 1\%$. The detection limit was calculated according to IUPAC rules (Long and Winefordner, 1983), and the sensitivity of the analytical conditions was also evaluated. Accuracy was checked with recovery assays, by adding known amounts of analyte and processing the mixtures as described above for amounts of analyte and by processing the mixtures as described above for experimental samples. Precision [relative standard deviation (RSD)] was also checked in six determinations of five different randomly chosen samples and was found to be between 1.8 and 9.0%. Recovery of $99.3 \pm 2.8\%$ was obtained by mean value SD of four determinations in two different samples. The detection limit of 1.8 pg and sensitivity were suitable for the range of Cr concentrations encountered and are compatible with estimates given by other authors. The technique was accurate and reproducible.

Chromium Concentrations in French Wine and Grape Samples. Chromium content ranged from 6.6 to 90.0 µg/L in red wines ($\bar{x} = 22.6$ µg/L), from 6.6 to 43.9 µg/L in white wines ($\bar{x} = 21.3$ µg/L), and from 10.5 to 36.0 µg/L in champagne ($\bar{x} = 25.1$ µg/L) (Table 2). Cr levels likely reflected differences in grape variety, environmental factors in the vineyard (e.g. soil, climate), and wine-processing techniques. Chromium content in

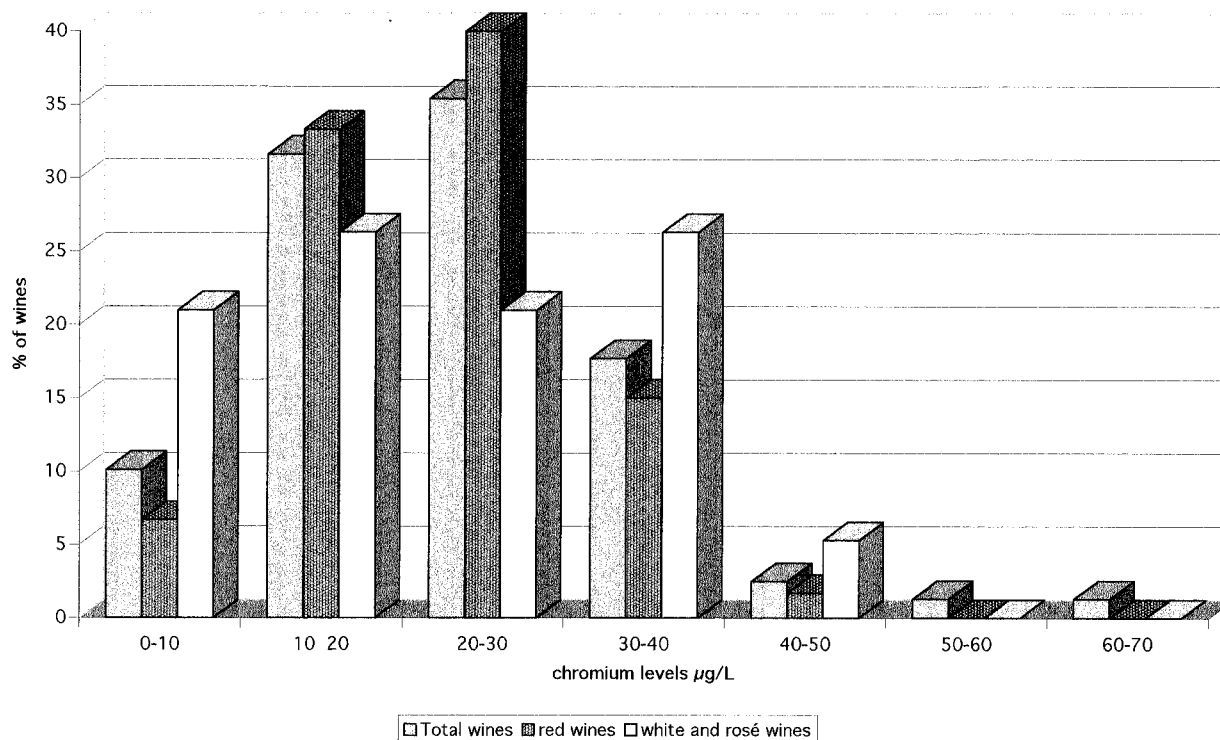


Figure 1. Chromium levels for red, white, and rosé French wines. The bars represent, from left to right in each grouping, total wines, red wines, and white and rosé wines.

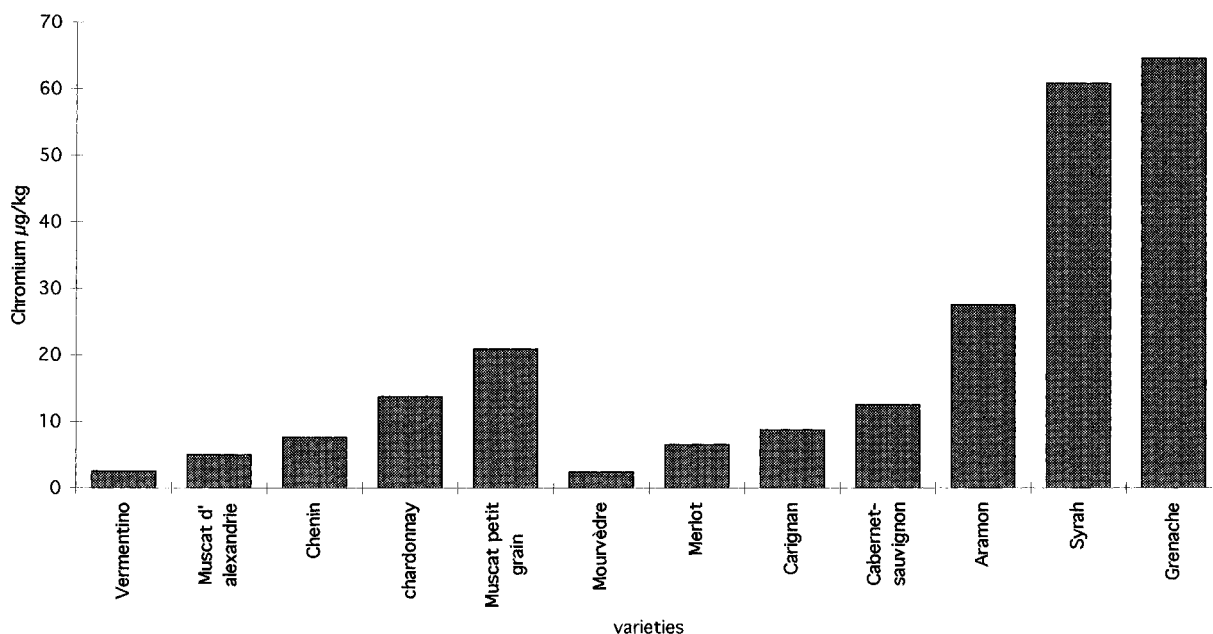


Figure 2. Chromium levels for white and red grapes of different varieties.

wine can also be connected with the nature of metallic oxides used for bottle pigmentation and the age of the bottled wine (Darret et al., 1986). On the basis of the analysis of chromium concentrations for different vintage wines of the same vineyard and winery, chromium concentrations significantly increase with the age of the wine ($r^2 = 0.750$, $p < 0.05$) (Table 3). This can be the result of contamination during storage by stainless steel or after bottling by chromium oxides used for pigmentation of the bottle during the aging process.

Chromium levels in 94% of all wines tested were < 40 $\mu\text{g/L}$ (Figure 1). Only 4% of all wines tested (5% for white and 2% for red) had Cr concentrations ≥ 40 $\mu\text{g/L}$ (Figure 1). In grape samples, chromium levels ranged

from 2.4 to 64.6 $\mu\text{g/kg}$. Cr levels were higher in red (64.6 $\mu\text{g/kg}$) than in white varieties (20.9 $\mu\text{g/kg}$) (Figure 2). Initial concentration of Cr in grapes can be increased or decreased by the successive technology steps involved in wine production (Etievant et al., 1988).

Estimation of Chromium Intake from Wine. It is important to monitor food and beverages for metallic elements that may be toxic when their concentrations exceed recognized safe levels. In France, alcoholic drinks represent 35% of the daily intake of beverages and are therefore an important source of several minerals. In France, alcoholic drink consumption is 481 mL/day, of which 305 mL is wine (Darret et al., 1986). Estimated chromium content in all alcoholic drinks

(wine, beer, cider, and liquor) is $1.3 \mu\text{g}/100 \text{ g}$ (Darret et al., 1986). This compares to Cr content of $0.3 \mu\text{g}/100 \text{ g}$ in water, $1.6 \mu\text{g}/100 \text{ g}$ in soft drinks, and $2.2 \mu\text{g}/100 \text{ g}$ in tea and coffee. Average Cr contribution of all drinks was estimated to be approximately 11%. In our study, estimated weekly intake of chromium from wine for the French population was estimated to be $28.4 \mu\text{g}$ per resident or $4.06 \mu\text{g}$ per day per resident on the basis of the official wine consumption rate of 66 L per year per resident (Boulet et al., 1995). In the United States total chromium dietary intake was estimated to be $23.1 \pm 2.9 \mu\text{g}/\text{day}$ for women and $38.8 \pm 6.5 \mu\text{g}/\text{day}$ for men (Anderson et al., 1993). If a similar Cr dietary intake in France is assumed, then wine may contribute up to 10% of daily total dietary Cr intake.

For comparison, mean chromium content in wine consumed by the Italian population was estimated to be 8.5 ± 6.0 (SD) $\mu\text{g}/\text{L}$, with concentrations ranging from 2.4 to $33.2 \mu\text{g}/\text{L}$. Estimated weekly intake of Cr in Italy from wine was estimated to be $17.0 \mu\text{g}$, assuming an individual consumption of 2 L of wine (Minoia et al., 1994). Estimated weekly intake of Cr from other beverages analyzed by these authors was minor (e.g. the Cr contribution of mineral water was $1.9 \mu\text{g}$). Our results show that estimated weekly intake of chromium from wine for the French population is 1.67 times more than for the Italian population. In Belgium, the average oral daily intake of chromium from food and beverages is about $10 \mu\text{g}$ to 5 mg (Buchet et al., 1983). In a recent survey on levels of Cr in a wide range of Canadian foodstuffs, concentrations ranged from nondetectable (i.e., $<0.004 \mu\text{g}/\text{g}$) in several foods to $0.1 \mu\text{g}/\text{g}$ in wheat and bran cereals (Hugues et al., 1994). Estimated oral intake of Cr in the Spanish diet is estimated to be 0.12 mg/day (Barbera et al., 1989). Our estimated daily intake of chromium from wine for the French population represents only 3.4% of daily total oral Cr intake in the Spanish diet.

These data indicate that wine can have a significant contribution to the dietary intake of chromium. The causes of differences in wine chromium levels, such as possible differences in soils, wine varieties, winemaking, conservation processes, and environmental pollution, should be further studied. A measure of the human absorption of this element after wine ingestion is also necessary to assess potential health effects.

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