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Received for review May 27, 1975. Accepted January 28, 1976.

Trace Element Analysis of Wine by Proton-Induced X-Ray Fluorescence Spectrometry

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Using proton-induced x-ray fluorescence spectrometry (PIX), nine trace elements have been simultaneously determined in representative wines from the San Joaquin Valley of California. With the exception of high copper content in two muscatels, all wines had low concentrations of the elements examined, and were within the ranges previously reported in wines. On the basis of these nine wines, no conclusions can be made as to patterns or trends of elemental composition between location sites or wine types, but further investigation by PIX, which is very well suited for wine analysis, seems warranted.

Trace element analysis of wine has long been of interest and concern to enologists. The deleterious effects on color, aroma, and taste of several metals, including copper, iron, zinc, nickel, tin, and aluminum, have been reviewed by Mrak et al. (1937), Mrak and Fessler (1938), Amerine (1958), Amerine et al. (1972), and Eschnauer (1974). Copper and iron, which contribute to haze formation and color defects in wine (Berg and Akiyoshi, 1956; Amerine et al., 1972), are monitored routinely as part of standard wine quality control tests. Nickel has also been shown to cause clouding in wines (Eschnauer, 1965b).

The trace element composition of grapes is influenced by the soil, by equipment used during vinification, and by wine processing treatments such as fining or filtration. It is further affected by the trace metals in insecticides, fungicides, or nutrients used in the vineyard and by environmental pollution. Because of concern over potentially toxic elements such as Pb, As, or Cd, these elements have also been surveyed in wine (Rankine, 1955; Eschnauer, 1965a; Edwards, 1973; Martina et al., 1973; Basile and Tarallo, 1974; Castelli et al., 1974; Garrido et al., 1974). Typical concentration ranges for selected elements in wines are shown in Table I. Maximum acceptable levels in wine for several metals as proposed by the Office International de la Vigne et du Vin (O.I.V.) for its member countries and by Canada and Germany are shown in Table II. More extensive reviews of the inorganic constituents in wine have been published by Amerine (1958) and Eschnauer (1974).

Determination of the content of any metal has typically been done by time consuming element-specific procedures. Amerine (1958) and Schneyder (1974) have surveyed the chemical determination procedures and atomic absorption techniques used in wine trace metal analyses. Because of the interest in the quantitative determination of several elements, such as copper and iron for wine stabilization control and lead or arsenic to monitor pollutants, the use of a multielement technique for the simultaneous analysis of many elements is desirable in wine analysis. Energy-dispersive x-ray fluorescence analysis has the advantage over its principal competitor, neutron activation analysis, that the elemental sensitivity is a smoothly varying function of atomic number Z . The proton-induced variant of x-ray fluorescence analysis (PIX) has its maximum sensitivity in the regions $25 < Z < 35$, which includes Cu, Fe, Zn, Ni, As, and $Z \sim 80$, including Pb. In this method accelerated charged particles serve to induce fluorescent x rays, the energy spectrum of which is then analyzed by a Si(Li) detector to identify and quantify the elements present. The choice of physical parameters for optimizing PIX analyses has been discussed by Herman et al. (1973) and application to analysis of biological materials is dealt with in detail by Campbell et al. (1975).

Wine is ideally suited for trace metal analysis by this technique. The elements are present in high enough concentrations to permit direct sampling of the wine without preliminary concentration steps. Furthermore, as a homogeneous and aqueous system, neither acid digestion nor ashing, which are generally required by atomic absorption procedures, is required for sample preparation. However, even in spotting a homogeneous solution such as wine, different thicknesses in the target may be produced and quantification assuming uniform cross-sectional

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Table I. Ranges of Trace Metal Content of Wines Reported in the Literature

Element	Concn, ppm	Origin of wine surveyed	Reference
Cu	0.04-0.48	California	Amerine, 1958
	0.13-2.50	South Africa	Zeeman and Butler, 1962
	0.0-0.10	Italy	Castelli et al., 1974
Fe	0.0-35.00	California	Amerine, 1958
	2.7-5.3	Russia	Venskevicus et al., 1973
	0.0-21.0	Italy	Castelli et al., 1974
Ni	0.0-1.10	Germany	Eschnauer, 1965c
Mn	0.25-2.2	Sicily	Corrao, 1963
	0.0-2.62	Italy	Castelli et al., 1974
	0.8-3.3	France	Peynaud, 1950
Zn	0.30-4.83	Germany	Deshusses and Vogel, 1962
	0.23-3.88	South Africa	Zeeman and Butler, 1962
Br	0.0-2.00	Italy	Guglielmi, 1953
Rb	0.22-1.00	France (white wines)	Bertrand and Bertrand, 1949a
	0.22-4.16	France (red wines)	Bertrand and Bertrand, 1949a
Pb	0.40-3.60 ^a	Ohio	Still and Fahey, 1963
	0.04-0.086	Australia	Rankine, 1955
	0.18-0.97	South Africa	Zeeman and Butler, 1962
	0.003-0.305	California	Edwards, 1973
	0.30-0.57	Italy	Castelli et al., 1974
As	0.40-3.93	Germany (musts)	von der Heide and Hennig, 1933
	0.22-2.32	Germany (wines from above musts)	von der Heide and Hennig, 1933
	0.0-0.03	Spain (musts and wines)	Garrido et al., 1974
	1.0-4.44 ^{a, b}	Ohio	Still and Fahey, 1963
Cd	1.30-4.10	Germany	Eschnauer, 1965a
	0.0-0.21	Italy	Castelli et al., 1974
Cr	7.3-8.7	Russia	Dobrolyubskii and Viktorova, 1973
	0.0-0.17	Italy	Castelli et al., 1974
Mo	0.6-13.2	Italy	Libero, 1968

^a Wine made from Concord grapes treated with PbAsO₃. ^b Calculated as AsO₃.

Table II. Maximum Acceptable Limits for Some Elements in Wine (Concentration in Parts per Million)

Element	Canada ^a	Germany ^a	O.I.V. ^b
As	0.2	0.2	0.2
B		14.0	14.0
Br		1.0	1.0
Cd		0.1	
Cu	2.0	5.0	
F	2.0	5.0	5.0
Pb	0.5	0.3	0.6
Sn		1.0	
Zn	5.0	6.0	

^a Schneyder, 1974. ^b Office Internationale Vigne Vin, 1972.

thickness (density) is prone to error. As discussed by Campbell et al. (1975) use of an internal standard and of a small target spot irradiated by a uniform proton beam eliminate this error, allowing accurate determination of element concentrations.

In this study, elements in California wines were quantified by PIX using both Sr and Cd for internal standards to permit a cross-check on the consistency of the results.

EXPERIMENTAL SECTION

Materials. Nine wines, including four experimental wines made by standard procedures at the University of California winery (wines A-D) and five commercial

samples (E-I), were selected for this investigation. Their codes and descriptions are listed in Table III.

Target Preparation. For each wine, several samples, to each of which two internal standards were added, were analyzed. Standard aqueous solutions (0.25 ml) having known concentrations of CdCl₂·2.5H₂O and SrNO₃ were added to 1-ml specimens of wines to provide spikes of 421 ppm of Cd and 71.6 ppm of Sr, respectively. Pipets fitted with medical grade polyethylene tubing were used to spot a droplet of wine on 20 μg/cm² carbon foils, which were then allowed to dry. The spots had diameters of less than 1 mm.

Proton-Induced X-Ray Fluorescence Spectrometry. PIX analyses were made on one set of samples (except D) as described previously by Campbell et al. (1975) using a proton beam current of ~0.2 μA. A typical x-ray energy spectrum of wine is shown in Figure 1. The accelerator was then shut down, maintenance was performed for 2 days, the machine switched on again, and the beam re-tuned. The second set of specimens was then analyzed with a 1-μA beam; this afforded a very stringent test of reproducibility. The trace metal contents from the two runs were calculated on the basis of both the Sr and the Cd internal standards using the equation:

$$\frac{C_e}{C_s} = \frac{X_e A_e \sigma_s \omega_s \epsilon_s}{X_s A_s \sigma_e \omega_e \epsilon_e}$$

Table III. Description of California Wines Analyzed by PIX

Code	Vintage year	Wine type	Grape variety	Location or origin of grapes
A	1966	Dry red table	Ruby Cabernet	Westside
B	1973	Dry red table	Ruby Cabernet	Westside
C	1967	Dry red table	Ruby Cabernet	Kearney Horticultural Field Station
D	1973	Dry red table	Ruby Cabernet	Kearney Horticultural Field Station
E	1949	Sherry	White blend	San Joaquin Valley
F	1968	Sherry	White blend	San Joaquin Valley
G	1974	Sherry	White blend	San Joaquin Valley
H	1959	Muscatel	Muscat of Alexandria	San Joaquin Valley
I	1970	Muscatel	Muscat of Alexandria	San Joaquin Valley

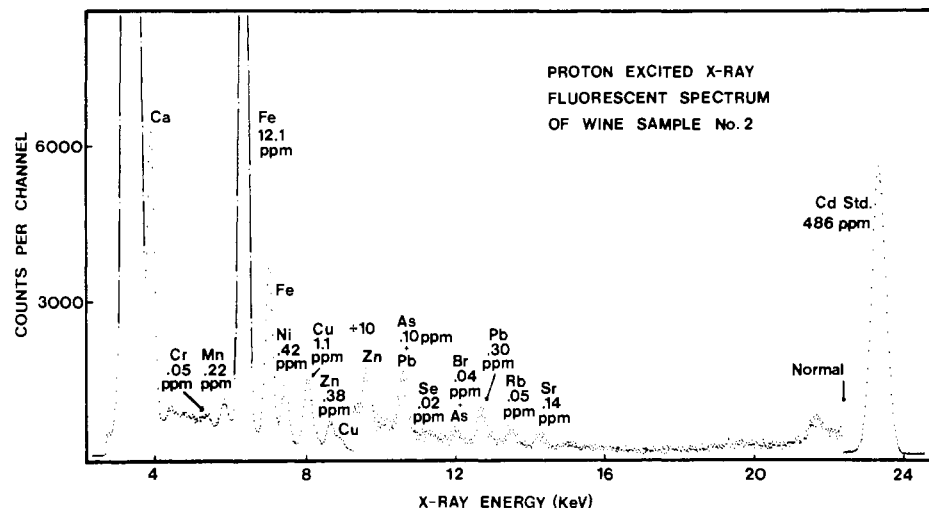


Figure 1. Typical proton excited x-ray spectrum of a wine (with Cd internal standard).

Table IV. Trace Metal Contents of Wine I^a Using Two Internal Standards

Element	Concn, ppm		Statistical error, 1 SD
	Sr standard	Cd standard	
Mn	0.747	0.788	± 0.03
Fe	1.562	1.647	± 0.05
Cu	0.730	0.769	± 0.03
Zn	0.904	0.952	± 0.03
Pb	< 0.083	< 0.087	
As	0.061	0.064	± 0.03
Br	0.417	0.439	± 0.04
Rb	1.007	1.062	± 0.08

^a Code defined in Table III.

Table V. Reproducibility for Trace Metal Analyses of Two Wines

Specimen ^a	Element	Concn, ppm ^b		1 SD
		Run 1 (0.2 μA)	Run 2 (1 μA)	
H	Mn	0.685	0.735	± 0.03
	Fe	2.120	2.128	± 0.06
	Cu	1.111	1.043	± 0.04
	Zn	0.413	0.440	± 0.03
	Rb	0.811	0.817	± 0.08
F	Mn	0.744	0.815	± 0.03
	Fe	1.598	1.538	± 0.05
	Cu	0.103	0.118	± 0.01
	Zn	0.668	0.528	± 0.04
	Rb	0.955	0.935	± 0.08

^a Codes defined in Table III. ^b Relative to the Sr standard.

where C = parts per million concentration, X = measured K (or L for Pb) x-ray intensity, A = atomic mass, σ = K ionization cross-section, ω = fluorescence yield, ϵ = Si (Li)

Table VI. Mean Trace Metal Contents^a of Nine California Wines (Concentration in Parts per Million)

Wine sample ^b	Fe	Cu	Mn	Ni	Zn	Br	Rb	Pb	As
A	4.10	0.35	0.99	0	1.08	0.40	0.70	0.12	0.10
B	4.09	0.22	1.09	0.02	0.69	0.54	1.54	0.14	0.11
C	1.53	0.08	0.56	0.01	1.67	0.22	0.93	0.13	0.06
D	2.25	0.24	1.64	0.14	0.31	0.47	2.81	0.06	0.02
E	2.28	0.17	0.84	0.01	1.99	0.19	1.54	0.04	0.02
F	1.60	0.10	0.74	0	0.67	0.14	0.96	0.07	0.05
G	0.41	0.03	0.18	0	0.26	0.44	0.58	0.07	0.06
H	2.18	1.14	0.71	0	0.43	0.19	0.83	0.09	0.07
I	1.61	0.75	0.77	0	0.93	0.43	1.04	0.09	0.06

^a Mean calculated from concentrations determined using Sr and Cd standards. ^b Codes defined in Table III.

detector efficiency, e denotes each element in the sample, and s denotes either standard element.

Statistical, systematic, and experimental errors contribute to the error in C_e . The x-ray intensities contribute statistical errors. The relative ω and ϵ values are known to within 1–3%, but different theories predict σ_s/σ_e ratios that differ by up to 10%, depending on the pair of elements compared. This latter uncertainty is the principal systematic error; it is decreased a little by using two internal standards of rather different Z . Experimental error will arise if the beam is nonuniform, does not cover the entire specimen, is unstable, or is sufficiently intense to volatilize some elements. One standard, Cd, is deliberately chosen for its ease of volatilization; loss of Cd due to excessive proton current would yield apparent concentrations higher than those given by the Sr standard.

RESULTS AND DISCUSSION

Consistency between Two Standards. Table IV shows results for one sample relative to the two standards. Results relative to Cd systematically exceed those relative to Sr by 5.5%. One might at first attribute this to Cd volatilization. However, in four specimens the Sr data were higher and in four the Cd data were higher. The factor between the two sets of data was constant for the eight elements observed in each sample, and ranged from 0.94 to 1.23 across the samples. There is therefore no evidence for serious losses of Cd. We attribute the observed effects mainly to volume errors incurred in solution preparation.

Other runs were carried out at currents ranging from 0.6 to 1.0 μ A. In these, losses of Cd were clearly observed.

Reproducibility. Since our main cause of experimental error is beam nonuniformity and instability, we regard the reproducibility test described above as much more stringent than merely running duplicate samples one after

the other in one experiment. By performing the second run at 1 μ A, we combined reproducibility and volatilization studies.

In the 1- μ A runs, losses of Cd, Pb, Br, and As were observed. We expected that Mn, Fe, Cu, Zn, and Rb would survive; they did, and their concentrations (given by the Sr standard) agreed well with those measured in the 0.2- μ A run. Representative results for two wines are given in Table V. Given that this is a preliminary study of concentrations typically 1 ppm, we find it extremely encouraging that the data should be reproducible within the statistical errors.

Trace Element Concentrations. The final results, collected in Table VI, are those from the 0.2- μ A run, averaged over the Sr and Cd standards. In one special case (D), accelerator problems forced us to use 0.8- μ A data. We believe systematic errors to be less than 10%, and the statistical errors (2 standard deviations) are as indicated in Tables IV and V.

None of the wines had unusual levels of any trace metal, as seen by comparing the metal content reports here (Table VI) with those of the literature (Table I). No wines contained any of the trace metal in levels exceeding tolerance limits as listed in Table II. The iron content of the nine samples is below the maximum level of 5 ppm recommended by Berg (1953). With the exception of wines A and B, all values for iron fall below 4 ppm, suggesting that the wines have all been treated for iron removal (Amerine et al., 1972). The levels of copper in the muscatels, wines H and I, were extremely high. Although H and I were clear, generally copper concentrations should be maintained below 0.2 to 0.4 ppm for the prevention of browning and haze formation (Amerine and Ough, 1974).

Although the rubidium contents fall within the range reported in the literature, there was no trend of higher Rb concentration in the red wines as previously reported by Bertrand and Bertrand (1949a). Higher concentrations of Rb have been reported in the skins and stems than in berry pulp (Bertrand and Bertrand, 1949b); consequently red wines made with longer skin contact time are expected to have a higher Rb content than white wines which have little or no skin contact.

For all of the wines, the lead content is low, well below the German tolerance limit of 0.3 ppm for Pb in wine (Schneyder, 1974). Arsenic contents were also below the 0.2 mg/l. tolerance limits as proposed by several countries in Table II. No limits for arsenic or lead in wine exist in the United States, but comparison of these values with the limits for lead or arsenic in drinking water, 0.05 ppm, suggests that no problematical levels of Pb or As exist in the wines investigated.

ACKNOWLEDGMENT

We thank J. A. Thompson and L. A. McNelles (University of Guelph) for their assistance and C. S. Ough

(University of California) for providing the experimental wines.

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Received for review October 6, 1975. Accepted January 26, 1976.