RADIOCHEMICAL ASSAY OF WOOD TREATED WITH CHROMATED COPPER ARSENATE PRESERVATIVES

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ABSTRACT

The assay of preservative-treated wood for chromium, copper, and arsenic, based on isotopic dilution with radioactive tracers, proved to be highly sensitive and precise. This safe technique provides a rapid and inexpensive means of quality control.

Additional keywords: Radiochemical assay, CCA wood preservatives, radioactive tracers, wood preservation, quality control.

INTRODUCTION

Water-soluble preservatives of high effectiveness containing arsenic, copper, and chromium that leave wood virtually odorless, clean and, when dry, paintable (Eaton 1957) are finding increased use to protect wood against decay fungi, insects, and marine borers. One difficulty, however, is determining the distribution of their components in wood, for standard assay procedures (AWPA 1973) are complicated and time-consuming; and they often require highly sophisticated laboratory facilities. Even though it appears that the three metallic salts—copper, chromium, and arsenic—do not separate during the passage of the treating solution across cell walls (Rudman 1966), it is advantageous to have at our disposal an assay process by which we can analyze for each of the three elements.

The analytical method now used for the three elements requires destruction of the wood with a mixture of nitric, sulfuric, and perchloric acids. This tedious method requires special attention because reproducibility of the results is subject to interference from other elements. The X-ray spectrographic method (DeBala and Wright 1965; Hartford 1971) gives satisfactory results, but the equipment is expensive, and preparation of a finely divided and homogeneous sample takes time. Spectrometric analysis through atomic absorption (Lambert 1969), though not as expensive as the X-ray method, is precise; but the sample must be homogenous and finely divided, and this is not easy. Colorimetric analysis (Hudson 1970) requires only a spectrophotometer and a small centrifuge. Neutron activation analysis requires an expensive nuclear reactor, but it is accurate and safe (Meyer and Siau 1972; Siau and Meyer 1970).

This paper describes an accurate, inexpensive, and safe method for assay of components of water-soluble preservatives that is readily adaptable to quality control. The techniques are based on radiometric analysis procedures proposed by Morrison (1965), Morrison and Freiser (1966), Sandell (1950), and Ruzicka and Stary (1968).

EXPERIMENTAL

Preparation of wood samples

Twenty 4-mm diameter cores were taken with an increment borer from untreated pine poles and from pine poles that had been pressure-treated with chromated copper arsenate, type A (CCA-A) (AWPA

1973). The outer 3.75 cm of each air-dried core was finely ground and placed in respective 250-ml round-bottom flasks with ground glass stoppers for untreated and treated wood. Twenty-five ml of a commercial sodium hypochlorite solution (TAP-S) with pH 11.5 was added to each flask. After magnetic stirring for 30 minutes at 60 C, the contents of each flask was filtered, washed with distilled water, and diluted to 100 ml in a volumetric flask.

Determination of chromium

A solvent extraction method for chromium was sought, and isoamyl alcohol with diphenyl carbazide as a complexing agent was chosen (Déon et al. 1969; Mathur and Behr 1967; Morrison 1965; Morrison and Freiser 1966; Sandell 1950). Both isotopic direct dilution (Bloch and Anker 1948) and double substoichiometric isotopic dilution (Ruzicka and Stary 1968) were applied to the extract using ^{51}Cr as a tracer. This isotope emits γ rays of 0.3201 Mev. It was found that under our laboratory conditions the double dilution techniques were better than direct isotopic dilution.

The double isotopic dilution technique was used in duplicate by adding to each of two aliquots of the extract a different amount of inert dichromate but the same amount of ^{51}Cr. Next a substoichiometric amount of complexing reagent was added; then each solution was extracted with the same amount of isoamyl alcohol.

Equal aliquots of the organic phase were taken immediately from each of the two samples and their activity was measured with a Na(Tl) scintillation well counter. A well counter improved the counting geometry and provided a high counting efficiency.

The data obtained from the well counter can be used in two ways to determine chromium:

1. *Standard curve method:* With a pipet we placed 1 ml of the untreated wood extract in three extraction funnels and added 1 ml of solution containing 0.003, 0.006, and 0.012 mg/ml of chromium as potassium dichromate respectively to each funnel.

Next we added 1 ml of a solution of arsenic pentoxide and copper sulphate in the same proportion as they are found in the CCA-A formulation (11% As, 33% Cu), and 1 ml of ^{51}Cr as chromate or dichromate with an activity of the order of 100,000 cpm/ml and of negligible concentration (1×10^{-9} mg or less). A pH of 0.7 was obtained adding 0.4N sulfuric acid, 1 ml of diphenyl carbazide (which always should be substoichiometric), and 5 ml of a saturated NaCl solution were added and the mixture was extracted with 5 ml of isoamyl alcohol after shaking 30 sec. We allowed the phases to separate, and 1 ml of the organic phase was taken to measure its activity with the scintillation counter. The standard curve was prepared by plotting the activity in cpm against the concentration of chromium.

We then combined 1 ml of the extract from the treated wood, followed the same procedure to obtain its activity, and used the standard curve to find the chromium concentration.

2. *Equation method:* When the number of chromium concentrations to be determined are few, the following procedure can be used. Two 1-ml aliquots from the treated wood extract with chromium concentrations of the order of 1×10^{-3} mg/ml or less were put in each of two separatory funnels. We added to one 0.0004 mg and to the other 0.0008 mg of chromium as potassium dichromate to act as the inert carrier. Then we added double-distilled water to a volume of 4 to 5 ml and 1 ml of ^{51}Cr with an activity of the order of 100,000 cpm/ml. We obtained a pH of 0.7 with 0.4 N sulfuric acid, added the diphenyl carbazide, and proceeded in the manner described above for the standard curve. Having obtained readings of two activites, we used the following equation (Ruzicka and Stary 1968) to determine the chromium concentration.

$$X \text{ mg of Cr in the aliquot} = \frac{0.0008A_2 - 0.0004A_1}{A_1 - A_2} \quad (1)$$

where:

A_1 = radioactivity of aliquot No. 1 in cpm/ml

A_2 = radioactivity of aliquot No. 2 in cpm/ml.

The difference in the radioactivity of the two aliquots is due to the variation in their specific activity.

Determination of copper

Spitzy's method (Braun and Tolgyessy 1967) based on the principle of indirect radiometric titration was used for the copper assay. The copper was extracted with an excess of dithizone solution in CCl_4; then we added a known amount of zinc solution labeled ⁶⁵Zn. This radioisotope emits beta rays of 0.325 Mev and gamma rays of 1.115 Mev. The excess dithizone reacts with the zinc solution and the residual activity was measured in the aqueous solution. pH was found to play an important role in relation to copper and zinc. Also, dithizone tends

to become oxidized and is transformed to diphenyl thiocarbodiazone, which is colorless and does not complex. The oxidation could be due to one or more of the following causes: oxidation by ferrous ions, especially in basic solution; low concentrations of halogens; light; or high temperatures. The dithizone solution should be prepared with very pure chemicals; otherwise the solution must be checked according to the procedure given in the following description of the determination of copper by the use of a standard curve.

1. *Standard curve method:* One ml of untreated wood extract was placed in each of four 125-ml separatory funnels, to which were added 0.1 ml of hydrazine (96% hydrate) and 1 ml of copper solution in concentrations of 0.002, 0.005, 0.007, and 0.01 mg/ml, respectively.

After a pH of 5 ± 0.1 with HCl and/or NH_4OH was reached, the extraction was
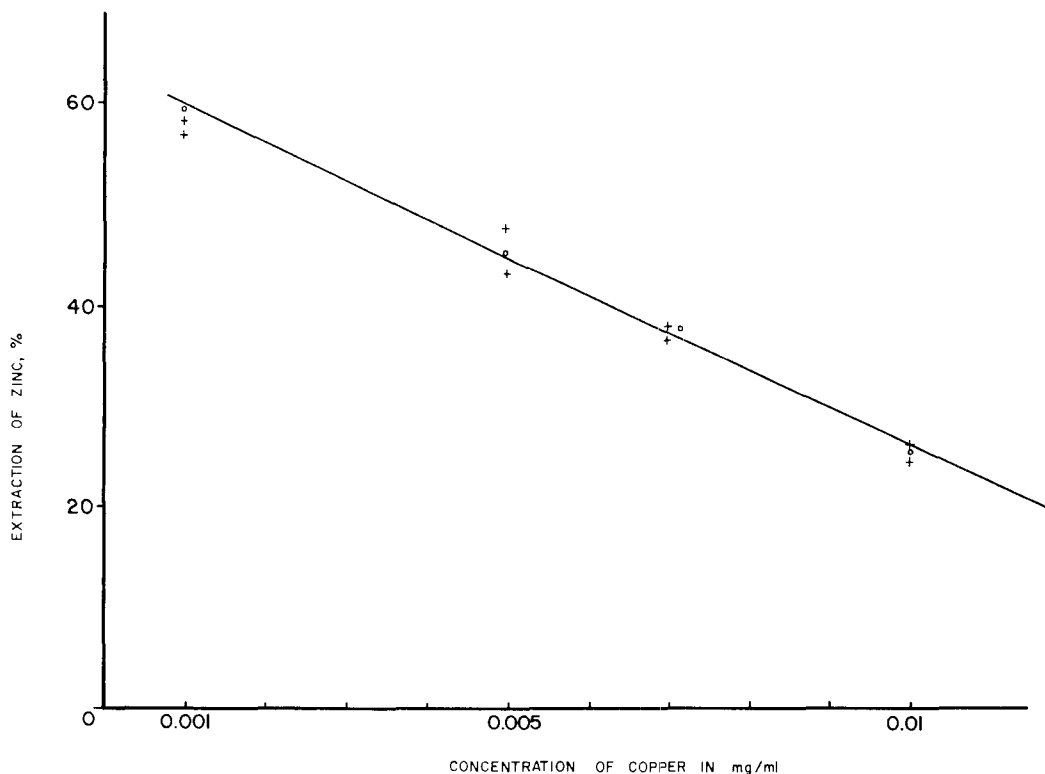

FIG. 1. Relation between percentage zinc extraction and copper concentration.
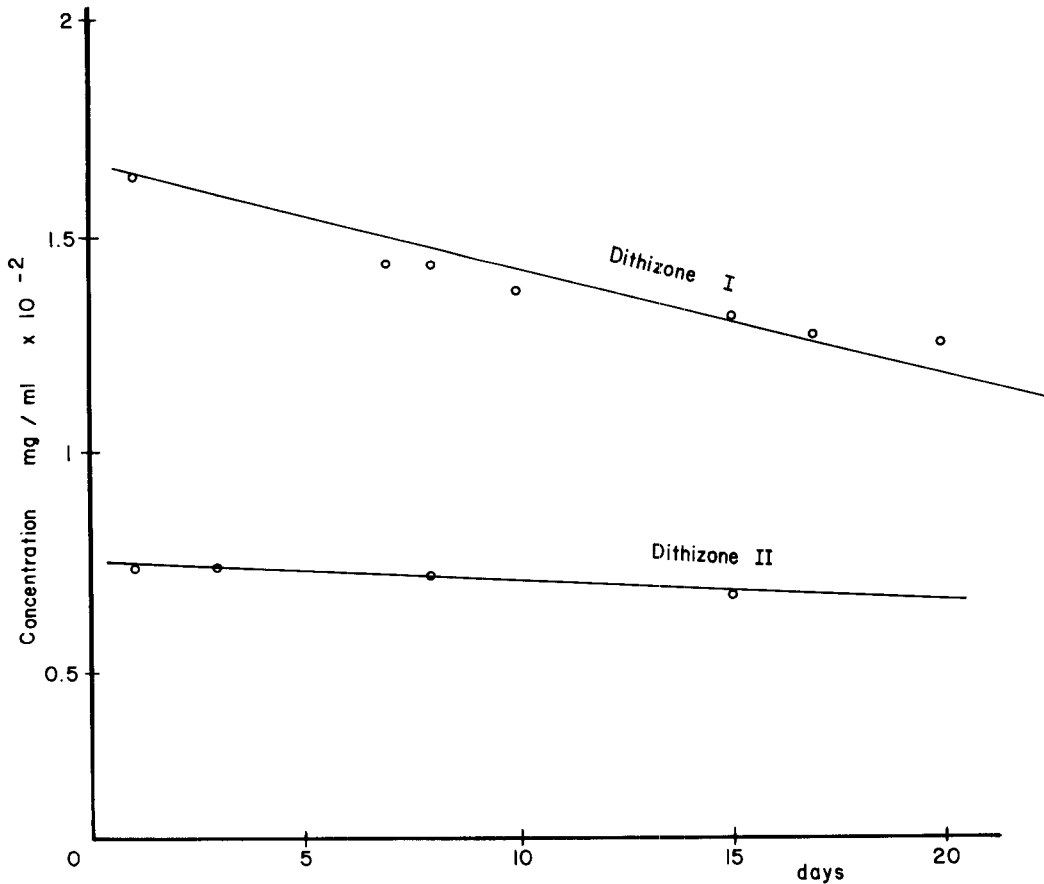
Fig. 2. Degree of oxidation of dithizone solutions with time.

made shaking 5 min with 6 ml of dithizone (0.07 mg/ml in carbon tetrachloride C.P.), and the phases were separated. To the aqueous phase we added 1 ml of standard zinc solution (0.066 mg/ml) and 1 ml of solution labeled with ^{65}Zn (from 100,000 to 200,000 cpm at a known concentration). The initial radioactivity of 1 ml of the solution (I_o) was measured with a well scintillation counter. This 1 ml of solution and the violet-colored organic phase were replaced in the funnel. We shook the mixture for 5 min again and the organic phase became purple. The phases were separated, and the radioactivity (I) of 1 ml of the aqueous phase was measured with the well scintillation counter. A graph was plotted showing the percentage of extraction of

zinc $(1 - I/I_o)100$ against the copper concentration in mg/ml (Fig. 1).

To check the dithizone solution, one can use any of the following procedures:

1. Each time that assay is to be done, a new standard curve with copper standard solution and a new dithizone solution should be prepared.

2. By measuring the oxidation of the dithizone solution with a spectrophotometer for example, the amount of dithizone added to the treated wood extract may be increased and the initial standard curve may be used.

The degree of dithizone oxidation can be observed in Fig. 2.

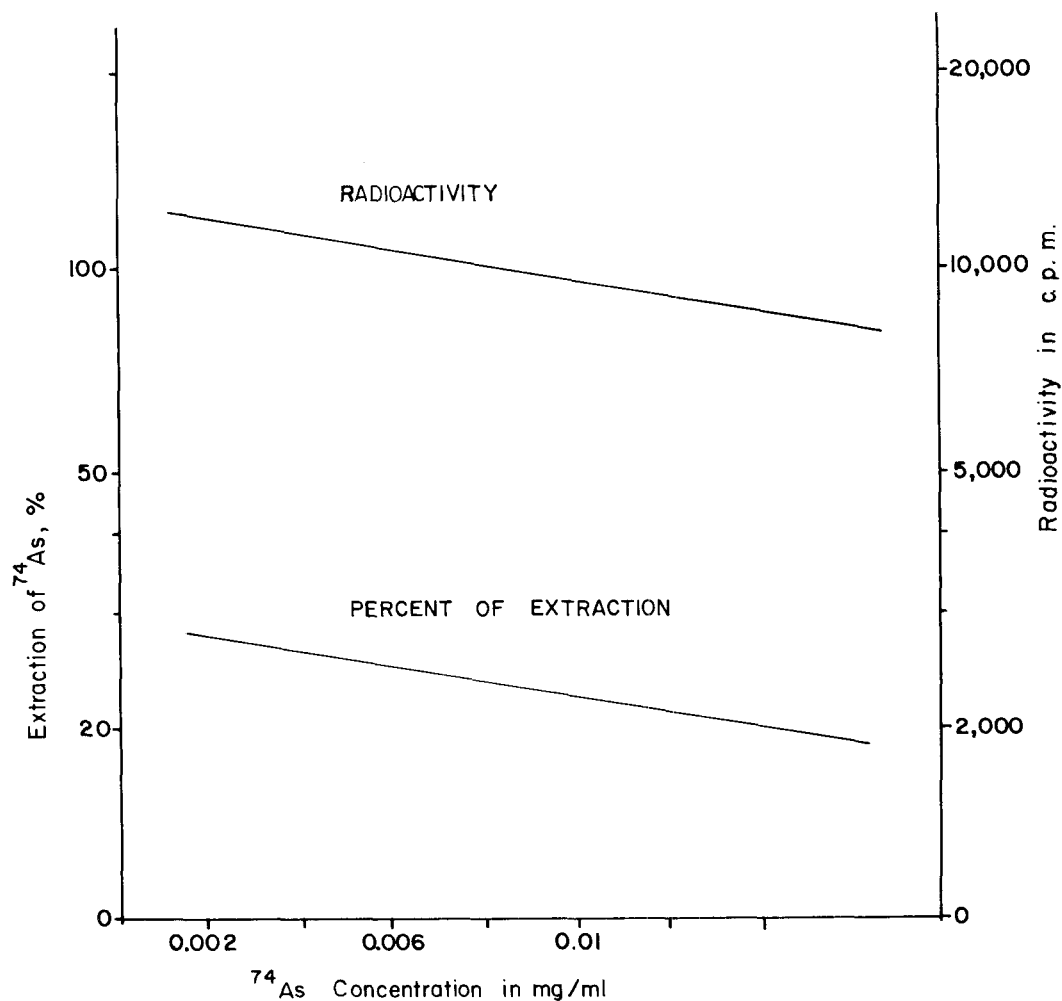Once the standard curve was prepared,

Fig. 3. Relationships between percent arsenic extraction with concentration, and radioactivty of the organic phase after extraction with concentration.

to an aliquot of the treated wood extract having a concentration of copper between 0.002 and 0.01 mg, we added 0.1 ml of hydrazine for each milliliter of the aliquot. A pH of 5 ± 0.1 was reached with 6N HCl and we continued in the same way as when we prepared the standard curve to determine the percentage of zinc. With this value we used the standard curve to determine the concentration of copper.

Determination of arsenic

We used n-butanol to extract the complex formed with sodium molybdate and

applied the principle of double substoichiometric dilution (Bloch and Anker 1948; Ruzicka and Stary 1968). This method was found to be more sensitive to impurities in air, water, containers, and reagents than for the determination of chromium. Because of these sources of error, we decided to prepare a standard curve to determine the concentration of arsenic in wood and not use Eq. 1.

When extracting the arsenic complex formed with sodium molybdate with n-butanol and measuring the optical density using a spectrophotometer at 370 mμ, we

TABLE 1. *Interference effect of copper and chromium on the extraction of arsenic using the isotopic dilution method.*

Sample No.	Concentration		Radioactivity of ^{74}As in 1 ml of the organic phase
	copper	chromium	
	mg	mg	cpm
1	0.000	0.000	2019 ± 45
2	0.009	0.015	1780 ± 42
3	0.019	0.031	1820 ± 42
4	0.081	0.051	1756 ± 42

TABLE 3. *Sensitivity of the isotopic dilution method used in the determination of chromium at five different concentrations.*

Given sample concentration, in mg of Cr*	Sample concentration found using the isotopic dilution method, in mg of Cr*
0.001	0.00099
0.002	0.00220
0.003	0.00310
0.010	0.01300
0.040	0.05700

*These results are the averages for three aliquots.

found it necessary to separate chromium because its presence resulted in false values. Chromium did not interfere when the double isotopic dilution method was used (Table 1).

Standard curve method: One ml of untreated wood extract and 1 ml of arsenic solution as As_2O_5 at concentrations of 0.002, 0.004, 0.006, and 0.01 mg/ml were placed, respectively, in four extraction funnels. Next we added to each funnel 1 ml of a solution of copper sulphate and potassium dichromate in the same proportions they are found in the CCA-A formulation 33% Cu, 56% Cr), and 5 ml of distilled water. The pH was adjusted to 7 ± 2 with HCl or NaOH. We added 1 ml of ^{74}As solution (this radioisotope emits beta rays of 0.9 and 1.5 Mev, and gamma rays of 0.63 Mev) with radioactivity of 300,000 cpm/ml and 1 ml of sodium molybdate water solution (0.5 g of sodium molybdate dissolved in 200 ml of distilled water, to which we added 84 ml of concentrated HCl and diluted to a volume of 500 ml), added 10 ml of n-butanol, and shook the funnels for

TABLE 2. *Decrease in the extraction power of sodium molybdate with time.*

Sodium molybdate samples	Radioactivity of ^{74}As in 1 ml of the organic phase (cpm)	
	day 1	day 28
15 mg	8609	5658
30 mg	16634	6746

1 min. The radioactivity of the organic phase was measured in cpm with the well scintillation counter, and the values were plotted against concentration of arsenic (Fig. 3).

With the standard curve prepared, we took an aliquot of the treated wood extract, adjusted its pH to 7, and added 1 ml of ^{74}As solution with a radioactivity of about 300,000 cpm/ml, 1 ml of sodium molybdate, and 10 ml of n-butanol. We shook the mixture for 1 min, then measured the radioactivity of 1 ml of the organic phase. With this value we determined the concentration of arsenic from the standard curve. A new standard curve should be prepared every few days because the half-life of ^{74}As is only 17.7 days.

One can also draw a graph of percent extraction $[(1 - I/I_o)100]$ against concentration, where I_o is the initial radioactivity from the aqueous phase in 1 ml of the sample and I is the final radioactivity for 1 ml of sample from the aqueous phase after extraction and separation. In this case the curve is useful for 8 days, after which a new sodium molybdate solution must be prepared since the extraction power of molybdate decreases with time. The rate of decrease was determined as follows: aliquots with 0.005 mg of arsenic were extracted initially with 15 and 30 mg of sodium molybdate and after 28 days; the radioactivities (cpm) obtained are shown in Table 2.

TABLE 4. Results of analysis of treated wood and commercial solutions of CCA preservatives obtained with the colorimetric method and the radiochemical methods.

Specimen	Analytical method	Retention (Pcf)		
		Cu_2SO_4	$Cr\,O_3$	$As_2\,O_5$
Wood core from pole 1 CCA-A treated	Colorimetric	0.065	0.270	0.097
	Radiochemical	0.073	0.220	0.092
Wood core from pole 2 CCA-A treated	Colorimetric	0.066	0.210	0.091
	Radiochemical	0.067	0.190	0.087
		Composition (%)		
CCA-A	Colorimetric	34	___	16
Solution	Radiochemical	34	___	15
CCA-B	Colorimetric	5.3 (CuO)	___	31
Solution	Radiochemical	5.3 (CuO)	___	31

RESULTS AND DISCUSSION

As shown in Table 2, sodium molybdate tends to lose its extraction power with time; thus after 28 days the sodium molybdate used in the determination of arsenic lost enough extraction power to introduce an error into the results, that if used without taking into account this characteristic.

The interference effect of copper and chromium in different amounts on the extraction of arsenic using the isotopic dilution method is for all practical purposes negligible, as shown in Table 1.

Table 3 shows at what sample concentration of chromium the isotopic dilution method used gave the best results. As can be observed, the method is most sensitive when the concentrations of chromium are between 0.001 mg and 0.003 mg.

So as to compare our proposed method with one already used, we determined the amount of Cu, Cr, and As in two wood cores and the percentages of Cu and As in commercial solutions of CCA-A and CCA-B preservatives, using our radiochemical methods and the colorimetric method. The data shown in Table 4 indicate that both types of methods gave essentially the same results.

Even though the results obtained are not based on extensive sampling and testing, they indicate that the radiochemical methods proposed in this paper are quite sensitive. In addition, they can be performed in less than 2 hr, the scintillation counter needed to measure the radioactivity is not expensive; the radioisotopes needed are easy to obtain and safe to use; and all other equipment needed is the usual found in most laboratories. The preparation of the sample for this method takes less than an hour, compared to the traditional method (acid digestion), which takes several days; and to prepare the finely divided and homo-

geneous sample needed for the X-ray method, several hours are needed. The size of the sample used in the radiochemical method is the smallest of all the other known methods, except for neutron activation analysis. Since the radioactivity of the elements used is very low, they do not represent safety problems, and only certain precautions must be taken such as the use of rubber gloves, laboratory coat, enameled trays, bulbs for the pipets, etc.

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