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Determination of Hexavalent Chromium in Extracts of CCA-Treated Building Timbers By Thermal Lens Spectrometry: A Comparison to Spectrophotometry and Atomic Absorption Spectrometry

M. Šikovec^a; F. G. Cruz^b; M. Franko^a; S. A. Katz^b

^a Jožef Stefan Institut, Ljubljana, SLOVENIA ^b Rutgers University, Camden, NJ, USA

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DETERMINATION OF HEXAVALENT CHROMIUM IN EXTRACTS OF
CCA-TREATED BUILDING TIMBERS BY
THERMAL LENS SPECTROMETRY:
A COMPARISON TO SPECTROPHOTOMETRY AND
ATOMIC ABSORPTION SPECTROMETRY

M. Šikovec^a, F. G. Cruz^b, M. Franko^a, and S. A. Katz^b

^aJožef Stefan Institut, 61111 Ljubljana, SLOVENIA

^bRutgers University, Camden, NJ 08102, USA

ABSTRACT

Thermal lens spectrometry was compared to spectrometry of the diphenylcarbazide chromophore and to atomic absorption spectrometry for the quantification of hexavalent chromium after extraction from CCA-treated building timbers with sodium carbonate-sodium hydroxide solution. Agreement among the results indicates that thermal lens spectrometry is applicable to the quantification of hexavalent chromium in this matrix.

INTRODUCTION

That the toxicities of hexavalent chromium compounds are greater than those of trivalent chromium compounds is well documented^{1,2}. To accurately assess the risks associated with exposures to environmental chromium, it is necessary to identify and quantify hexavalent chromium in a variety of natural and anthropogenic matrices. Recent attentions have focused on the determination of hexavalent chromium in airborne particulates^{3,4}, surface waters^{5,6}, soils^{7,8}, and various consumer products^{9,10}. Atomic absorption spectrometry (AAS) and spectrophotometry of the diphenylcarbazide chromophore (SPEC) are among the techniques applicable to quantifying hexavalent chromium in these matrices. However, features such as the non specificity of AAS for hexavalent chromium and the

relatively low sensitivity of SPEC in comparison to other methods sometimes limits the applicability of these two techniques. Therefore, the development of new analytical techniques with improved selectivity and sensitivity is important to the identification and quantification of hexavalent chromium. Thermal lens spectrometry (TLS) is such a technique that has been applied recently to the determination of chromium species¹¹⁻¹³.

TLS is based upon the indirect measurement of absorbance by "thermal lens effects". This phenomenon is a result of the heat generated in an irradiated sample by the non-radiative relaxation of absorbed energy¹⁴. When a laser beam with a Gaussian profile is used as the excitation source, the energy deposited in the sample results in the formation of a symmetrical radial temperature distribution. The temperature is the highest in the center of the irradiated volume. A lens-like element is formed in the irradiated sample as a consequence of the refractive index gradient, and the intensity profile of the laser beam changes accordingly. The relative change in the center beam intensity is a direct measure of the thermal lens strength which is proportional both to the absorbance by the sample and to the power of the laser beam. By using a adequate laser power, absorbances on the order of 10^{-7} absorption units have been measured by TLS¹⁵⁻¹⁷. In spite of this potential for enhancing sensitivity, TLS has not yet found wide application to routine analysis. One reason for this could be a lack of validating studies comparing TLS with other spectrometric techniques. The following work was undertaken to verify the reliability of TLS by determining hexavalent chromium in extracts of CCA-treated building timbers and comparing the results to those obtained by some other techniques; AAS and SPEC.

EXPERIMENTAL

Extraction of Timber Specimens

The collection and preparation of CCA-treated building timbers for determination of their hexavalent chromium contents has been described earlier¹⁸.

Replicate 100 mg specimens of each prepared timber sample were extracted by overnight shaking with 10 mL of 3 % sodium carbonate - 1 % sodium hydroxide solution at room temperature. Parallel extractions were performed on timber specimens spiked with 50 μg of Cr(VI). The concentrations of hexavalent chromium in the extracts were determined by TLS, SPEC, and AAS as described below.

TLS Measurements

The TLS measurements were made with a dual beam (pump/probe configuration) thermal lens spectrometer shown schematically in figure 1. A 50 mW air-cooled, argon-ion laser (Omnichrome) operating at 514.5 nm was used as the excitation source (pump beam). The pump beam was modulated at 8 Hz with a variable speed mechanical chopper (Scientific Instruments, Inc. model 300) and focused on to the sample cell holder with a 100 mm focal length lens. A He-Ne laser (Uniphase model 1103P) provided the probe beam. Collinear propagation of the pump and probe beams was obtained by a dichroic mirror. A second lens was used to increase the radius of the probe beam at the detector to facilitate sampling its intensity at its center. The fluctuations in the probe beam intensity were detected with a silicon photodiode (Laser Components model OSD 5-E) located 1.4 m from the sample cell. A red filter and a horizontal slit were located between the sample cell holder and the photodiode. The output of the photodiode was fed to a lock-in amplifier (Stanford Research model SR510) connected to a personal computer.

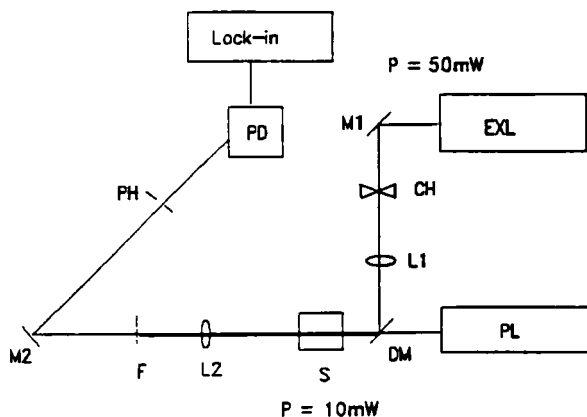


FIGURE 1:

SCHEMATIC DIAGRAM OF THERMAL LENS INSTRUMENT (EXL, EXCITATION LASER; PL, PROBE LASER; CH, CHOPPER; L1 L2, LENSES; DM, DICHROIC MIRROR; M1 M2, MIRRORS; S, SAMPLE; F, FILTER; PH, PIN HOLE; AND PD, PHOTO DIODE)

The sample or standard solution (10 mL) was neutralized, and then treated with 0.8 mL of solution containing 100 mg 1,5-diphenylcarbazide/10 mL acetone. Measurements were made after adding of 0.4 mL of solution containing 20 g 95 % sulfuric acid diluted with 80 mL water and allowing 20 minutes for color development¹⁹.

SPEC Measurements

The SPEC measurements were made with a Cary Model 16 spectrophotometer at a wavelength of 540 nm in 1 cm quartz cells. The extracts and standards (10 mL) were neutralized with dilute sulfuric acid, treated with 1 mL of 1 % (m/v) 1,5-diphenylcarbazide in acetone and 1 mL of 1 % v/v sulfuric acid, and allowed to stand for 10 minutes prior to the absorbance measurement²⁰.

AAS Measurements

The AAS measurements were made with a Varian Model 252 spectrometer at a wavelength of 359 nm in a rich nitrous oxide-acetylene flame. The absorbances of the

extracts were recorded, and their chromium contents were quantified by comparison to the absorbances of hexavalent chromium standards in the same sodium carbonate - sodium hydroxide matrix.

RESULTS AND DISCUSSION

The results of TLS measurements made on extracts from specimens of CCA-treated timbers are compared to those made by SPEC in table 1.

The results tabulated below reflect low recoveries from the specimens spiked with 50 μg of hexavalent

TABLE 1: HEXAVALENT CHROMIUM FOUND IN SPIKED SPECIMENS OF CCA-TREATED BUILDING TIMBER DETERMINED BY TLS AND SPEC

specimen	TLS, μg	SPEC, μg
TBE-o/1a	2.2 \pm 0.1	8.4 \pm 0.3
TBE-o/1b	0.55 \pm 0.04	2.90 \pm 0.09
TBE-o/2a	3.3 \pm 0.2	6.3 \pm 0.2
TBE-o/2b	0.64 \pm 0.04	4.5 \pm 0.1
TBE-i/3a	26 \pm 1	34 \pm 1
TBE-i/3b	21.6 \pm 0.9	‡
TBE-i/4a	26 \pm 1	29.3 \pm 0.9
TBE-i/4b	18.5 \pm 0.9	‡
FBF-o/5a	19.8 \pm 0.8	24.9 \pm 0.7
FBF-o/5b	9.4 \pm 0.4	‡
FBF-o/6a	18.1 \pm 0.7	21 \pm 0.6
FBF-o/6b	10.4 \pm 0.4	‡
FBF-i/7a	9.3 \pm 0.5	16.1 \pm 0.5
FBF-i/7b	9.5 \pm 0.5	20.1 \pm 0.6

Results for specimens designated b were determined from repeat measurements of those designated a 24 hours later.
‡ Parallel replicate specimen was not measured by SPEC.

chromium. These inconsistencies may be attributed to differences in conditions during or following the extraction which could result in: reduction of a part of the chromium spike, complexation of chromium with organic

ligands, and/or precipitation of chromium by organic or inorganic components of the extraction or chromophoric agents. These possibilities, especially reduction, are probably more significant when the extractions are performed at elevated temperatures as was the case with specimens TBE-o/1a and b and TBE-o/2a and b which were extracted at 120° C. In addition, decreases in hexavalent chromium concentration with time were observed. This is demonstrated by comparison of results for the specimens designated a with those designated b in Table 1. The latter were determined from measurements made 24 hours after the those from which the former were determined. Optimization of the extraction/quantification procedure was the objective of another work¹⁸, and spike recoveries of $100 \pm 5 \%$ were obtained when atomic absorption measurements were made immediately after the extraction.

Low spike recoveries notwithstanding, the results tabulated above provide a good basis for the comparison of results from TLS measurements with those obtained from SPEC measurements. In general, the results obtained by SPEC tend to be higher than the corresponding values obtained by TLS. For samples TBE-i/3, TBE-i/4, FBF-o/5, and FBF-o/6, the differences between the results obtained by TLS and those obtained by SPEC range from 13 to 29 %. The differences exceed 100 % in results for specimens with lower hexavalent chromium concentrations: TBE-o/1, TBE-o/2, FBF-i/7, and FBF-i/8. These differences are attributed to turbidity of the extracts. Typically, the turbidity contributed between 0.0180 and 0.0620 to the absorbance measured by SPEC. The contribution was not sufficiently reproducible to allow corrections by blank subtraction.

Light scattering processes caused by turbidity influence results obtained by SPEC measurements to a much greater extent than they influence those obtained from

TLS measurements. The reason for this lies in the origin of the TLS signal; i.e., the change of intensity in the center of the probe laser beam is directly proportional to the power of the laser beam (P):

$$\Delta I/I = [1.21A(-dn/dt)P]/\lambda k$$

where $\Delta I/I$ is the relative change in the probe beam intensity, A is the absorbance of the sample, dn/dt is the temperature coefficient of refractive index, λ is the probe beam wavelength, and k is the thermal conductivity of the absorbing solution. The TLS signal is linearly reduced by the loss in laser power due to the scattering of light. On the other hand, the loss of light intensity due to turbidity in SPEC measurements corresponds to from 4.1 to 13.3 % when the contributions of 0.0180 to 0.0260 are considered. By analogy, the TLS signals should be relatively lower by the same extent compared to signals expected in the absence of light scattering, and the relative error should be approximately the same for all TLS results regardless of the hexavalent chromium concentration in the extracts. Light scattering also affects the probe beam, but his effect is the same before and during the pump laser excitation. Consequently, light scattering has no influence on the final signal. In addition, the higher sensitivity of TLS required that all of the extracts be diluted by a factor of 5 which reduced the blank absorbances to values between 0.0040 and 0.0120. As a result, the concentrations of hexavalent chromium determined by TLS were reduced by only 1.0 to 2.8 % by the loss of laser pump power. Such reductions of TLS signals are small compared to experimental errors of 5 % typically associated with this technique.

The results obtained by TLS are expected to be more reliable than those obtained by SPEC. These expectations were confirmed when the performance of TLS was compared to AAS. This comparison is demonstrated in Table 2. These

TABLE 2: HEXAVALENT CHROMIUM CONCENTRATIONS IN SPECIMENS OF CCA-TREATED BUILDING TIMBERS DETERMINED BY TLS AND AAS

specimen	TLS, $\mu\text{g/g}$		AAS, $\mu\text{g/g}$	
TBE-o/9	55	± 2	54	± 0
TBE-o/9'	58	± 2	57	± 0
TBE-i/10	51	± 2	51	± 4
TBE-i/10'	42	± 2	42	± 1
FBF-o/11	34	± 2	34	± 4
FBF-o/11'	36	± 2	36	± 4
FBF-i/12	7.5	± 0.5	8.0	± 2

results were obtained by determining the hexavalent chromium concentrations of unspiked CCA-treated timber specimens from measurements on extracts obtained under optimized conditions¹⁸. The tabulated data reflect consistently good agreement between the results obtained by TLS and those obtained by AAS. More important than the differences between the two techniques which result from experimental errors are the differences between replicate determinations for the same specimens indicated as /1 and /2. The small differences between observed for replicate determinations are due to small inconsistencies in the extraction procedure.

Regardless of the discrepancies between the replicates, it is evident that the concentrations of hexavalent chromium are higher in the specimens from the outside surfaces (o) of the CCA-treated building timbers than they are in the specimens from their interiors (i). The differences between "o" and "i" specimens are more evident in the FBF timber sample. The differences between the TBE and FBF timbers are attributed to differences in dimensions and structure.

CONCLUSIONS

This investigation revealed that SPEC was not suitable for the determination of hexavalent chromium in

CCA-treated building timbers because the turbidity of the alkaline extracts interfered with conventional measurements of absorbance. Because TLS absorbance measurements are based on a different concept, photothermal effects, were are less affected by light scattering from turbidity. The advantages of TLS over SPEC have been demonstrated by others^{21,22}. The selectivities of the techniques for chromium are equivalent; Both are based on the diphenylcarbazide chromophore. In addition to higher sensitivity than SPEC for hexavalent chromium, TLS has lower limits of detection¹² (LOD = 0.2 ng Cr(VI)/mL).

The results presented in Tables 1 and 2 are a first attempt to compare TLS to more commonly-used, validated techniques. The use TLS for the determination of hexavalent chromium in CCA-treated building timbers is validated by the good agreement between results obtained by TLS and those obtained by AAS. In addition to high sensitivity, TLS has high selectivity for hexavalent chromium as the diphenylcarbazide chromophore. In the case of hexavalent chromium determinations in CCA-treated building timbers, sufficient selectivity with respect to trivalent chromium is provided by alkaline extraction¹⁸. In this case, quantification by TLS does not offer significant advantages over quantification by AAS. However, TLS has clear advantages over AAS for the quantification of hexavalent chromium in the presence of trivalent chromium in aqueous environmental matrices such as surface and ground water, wastewater, soil and waste leachates, et cetera.

Additional work is needed to confirm TLS as a reliable and accurate analytical technique. As a part of such endeavors, measurements of hexavalent chromium in a water SRM are in progress. These validations coupled with developments in laser technology are important factors in the promotion of TLS for routine chemical analysis and

for the identification and quantification of various chemical species at trace concentrations.

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