

An Evaluation of the Use of Near Infrared (NIR) Spectroscopy to Identify Water and Oil-borne Preservatives

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Abstract: In this research we experimented with a new and rapid way of analyzing wood. Near Infrared (NIR) spectroscopy together with multivariate analysis is becoming a widely used technique in the field of forest products especially for property determination and is already firmly established in the pulp and paper industry. This method is ideal for the chemical analysis of wood, and therefore preservative-treated wood.

Several commercially treated deckboards were obtained for this study: CCA/Hem-Fir; CCA/Eastern Hemlock; ACZA/Douglas Fir and ACQA-Hem-Fir. They were milled and scanned with a NIR spectrometer. Visually, the NIR spectra appear very similar, however when incorporated into the multivariate software; differences start to emerge. This software applies multivariate statistical techniques to the spectra, identifying chemical changes in the wood that are caused by preservatives. The samples separated out according to treatment and were easily distinguishable. Additionally, the technique was able to determine the preservative retention levels present. Two oil-based preservatives were also studied: Copper Napthenate and Oxine Copper. Again these samples separated and clustered according to their treatments. Furthermore with the Copper Napthenate samples, there was a clear graduation in solution strength.

This technique is rapid, non-destructive, portable and relatively low cost. It appears to have the potential for identifying both inorganic preservatives (those that contain copper, chromium or arsenic) and organic (carbon based) preservatives. The results clearly demonstrate that this technique has potential for use in a variety of recycling and sorting applications.

Introduction

The recent EPA announcement of the decision by treated wood manufacturers to voluntarily phase out the use of CCA-treated wood from virtually all residential applications by the end of 2003 (EPA 2002) means the use of arsenic-free alternatives such as ACQ and CBA in these applications is expected to greatly increase. Meanwhile CCA-treated wood no longer in service is still often mixed with C&D waste that also contains untreated wood, and once it has been weathered or painted, it is difficult for the homeowner, contractor, or local solid waste facility to visually differentiate the treated from the untreated wood. This causes problems in the waste stream; the presence of arsenic severely restricts the recycling possibilities of untreated waste wood.

Thus the need for sorting technologies to distinguish between CCA and non-CCA treated waste wood. Solo-Gabriele undertook a large feasibility study in Florida into on-line sorting technology for CCA-treated wood (Blassino *et al.* 2002). Detectors based on laser-induced breakdown spectroscopy (LIBS) and X-ray fluorescence (XRF) spectroscopy were able to quickly and accurately differentiate CCA-treated wood from other wood types in the C&D wood waste stream. Rapid detection methods for organic preservatives have also been studied (Schroder *et al.* 1998) using ion mobility spectrometry (IMS) in which a battery-powered IMS device coupled with a thermal desorption chamber successfully analyzed small pieces of treated wood for preservatives.

A method is needed for the rapid, inexpensive and reliable identification of wood that has been treated with preservatives. One possible method is near infrared (NIR) spectroscopy together with multivariate analysis (MVA). This has potential for detecting and distinguishing wood treated with both organic and inorganic preservatives, and is becoming a popular technique for the study of the properties of wood (Hoffmeyer and Pedersen 1995; Thumm and Meder 2001) and its composites (Rials *et al.* 2002, Engstrom *et al.* 1998). Principal component analysis (PCA) of NIR spectra has been successfully applied to the study of pulp characteristics and processes (Wallbacks *et al.* 1991) as well as the classification of various wood species (Schimleck *et al.* 1996). Although there has been much research into the classification and

prediction of chemical properties, little has been published with regards to wood preservatives. One paper (Feldhoff *et al.* 1998) has used NIR for the detection of inorganic preservatives in timber, however no multivariate analytical methods were applied. Preservative identification was based on differences in absorption from certain peaks in the spectra.

Materials and Methods

This study evaluated the ability of NIR spectroscopy to identify both water- and oil-borne preservatives. Three types of water-borne preservatives were chosen: CCA, ACZA and ACQ. Several commercially treated deck boards were obtained for each of the following preservative/wood species combinations: CCA/Hem-Fir (CCAHF), ACZA/Douglas-fir (ACZA) and ACQ/Hem-Fir (ACQ). In addition, East Hemlock boards obtained from northern Wisconsin were pressure-treated with CCA using laboratory equipment (CCA EH). Each deck board was cut into shorter boards, from which sections of wood were removed from the outer (0-5 mm) and inner (5-15 mm) assay zones and milled to pass through a Wiley mill 30 mesh screen. For the CCA EH samples, an additional “core” assay zone was cut from the center of the boards. The number of samples in each set is shown in Table I. All samples were analyzed for copper, chromium, zinc and arsenic using a standard laboratory method of digestion followed by atomic absorption spectroscopy (AWPA 1995). Two types of oil-borne preservatives were used: copper naphthenate and oxine copper. These were milled to the same standard as the water-borne samples.

Near Infrared Spectroscopy. The NIR measurements were made using a Nexus model 670 FTIR spectrometer (Thermo Nicolet Instruments, Madison, WI) at wavelengths between 1000-2500 nm. The NIR spectra were collected by embedding a fiber optic probe into a bag of the milled samples. Forty scans were collected and averaged into a single spectrum. Two spectra were recorded for each sample at different locations within the mixture.

Multivariate Analysis. Multivariate analysis of the data was performed using the Unscrambler (vsn. 7.5) software, CAMO, Corvallis, OR. Multiplicative scatter correction (MSC) was applied to the spectra prior to multivariate analysis using the same software. Principal component analysis (PCA) was used to observe any clustering and/or separation within the sample sets. The result from a PCA analysis is typically displayed in the form of a scores plot. The scores are the coordinates of the objects in a coordinate system defined by the directions of maximum variance, the principal components. The most commonly used scores plot is that for the scores vectors from PC1 and PC2. These represent the two largest variations in magnitude within the data. Partial least squares (PLS) analysis was conducted on the spectra after averaging. In each sample set, two thuds were used for calibration to create the model and the rest used for the validation set to test the model. Models were generated using full cross validation (Martens and Naes 1991). A summary description of the PLS technique can be found in an earlier paper (Rials *et al.* 2002) while a complete description of MVA can be found elsewhere (Martens and Naes 1991; Massart *et al.* 1998).

Results and Discussion

The sample sets were visually examined prior to the collection of NIR spectra. A range of colors was evident between and within sample sets. However the wavelength range for the NIR spectra collection was 1000–2500 nm avoiding the low wavelength visible region, thus preventing much of the masking of information within the NIR region. Two spectra were collected for each sample with Figure 1 showing a typical spectrum from each sample set. The spectra appear to be very similar except at lower wavelengths (closer to the visible region).

Spectral differences cannot be visually observed in Figure 1, however the application of multivariate analysis to the spectra allows hidden relationships and/or differences to be revealed. Principal component analysis (PCA) was performed on the sample set combinations shown in Table I. Figure 2 shows the scores plot resulting from the Water-borne sample set. Although there is some overlap, clusters were evident, showing some clear differences between the NIR spectra obtained from the individual sample sets. Differences between the CCA East Hemlock and CCA Hem-Fir samples were obscured by the magnitude of the variation between the ACQ Hem-Fir and ACZA Doug Fir samples.

The spectra were thus broken down into a CCA (East Hemlock and Hem-Fir species) and a Hem-Fir sample set (CCA- and ACQ-treatments) to enhance the differences observed in Figure 2. The PCA scores plot for the CCA samples (Figure 3) clearly shows groupings for CCA Eastern Hemlock and CCA Hem-Fir with separation along principal component 2 (PC 2). More importantly, the Hem-Fir samples in Figure 4 show much clearer separation between the ACQ and CCA treatments along PC 1, indicating that the treatment is playing a larger role in the sample separation than the wood species.

PCA was performed on the four individual sample sets, clustering was observed in terms of assay zone location. Figure 5 is a PCA scores map for CCA Hem-Fir, in which the samples separated into inner and outer assay zones on the negative and positive side of PC 1 respectively. This trend was similarly observed in the other sample sets. The inner and outer assay zones differ in terms of their treatment level; the inner assay zones generally have lower levels of preservative due to the depth of penetration. This was observed in the atomic absorption spectroscopy results (not shown). Even within the same assay zone, there is a graduation of treatment level with the higher preservative levels more positive along PC 1.

Partial least squares (PLS) regression was performed on the NIR data to predict the preservative retentions for the water-borne samples. PLS-1 regression was used on the samples where there was only one common retention type present while PLS-2 regression was carried out on the CCA samples to determine the CrO_3 , CuO and As_2O_5 retention levels. The types of preservative retention and regression used are listed for each sample set in Table 11. However, only results of particular interest and those which are representative have been presented. The results from a PLS-1 regression on the Water-borne sample set for CuO is shown in Figure 6 in which the NIR-predicted CuO retention is plotted against the actual CuO retention. It is clearly observed that both the calibration and validation sets fit well to the dotted equivalence line. The correlation coefficients (R^2) for calibration and validation were very high at 0.95 and 0.93 respectively and using only four PCs. A PLS-2 regression on the CCA samples produced similarly good correlations for CuO , CrO_3 and As_2O_5 retentions (not shown).

Retention values for the oil-borne samples were not available and thus no PLS regression was carried out. However, PCA was performed and the results are shown in Figure 7. There is a clear demarcation between the copper naphthenate and oxine copper samples. Looking closer, only at the copper naphthenate (Figure 8), the samples separate out in order of solution strength.

Conclusions

The results of this evaluation clearly show that near infrared (NIR) spectroscopy in conjunction with multivariate analytical techniques have the potential to identify and classify various preservative treatments applied to wood and also the level of preservative present. This technique has been further extended to organic preservatives and shown to be equally promising. This is being presently extended to treated solid lumber and the results compared with that obtained from the milled equivalent.

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Table I. Summary description of sample sets.

Sample Set	No. of Samples	Constituents
Water-borne	165	CCAHF, ACQ, ACZA, CCAEH
CCA	85	CCAHF, CCAEH
Hem-Fir	80	CCAHF, ACQ
CCA Hem-Fir	40	CCAHF
ACQ Hem-Fir	40	ACQ
ACZA Doug Fir	40	ACZA
CCA East Hemlock	45	CCAEH
Oil-borne	40	CuNap, OxCu
Copper Napthenate	28	CuNap

Table II. Summary of regression variables (preservative retentions) used for PLS modeling for each sample set.

Sample Set	Preservative Retention			
	CuO	ZnO	CrO ₃	As ₂ O ₅
Water-borne	×	-	-	-
CCA ^b	×	-	×	×
Hem-Fir ^a	×	-	-	-
CCA Hem-Fir ^b	×	-	×	×
ACQ Hem-Fir ^a	×	-	-	-
ACZA Doug Fir ^b	×	×	-	×
CCA East Hemlock ^b	×	-	×	×

^a PLS-1 algorithm^b PLS-2 algorithm

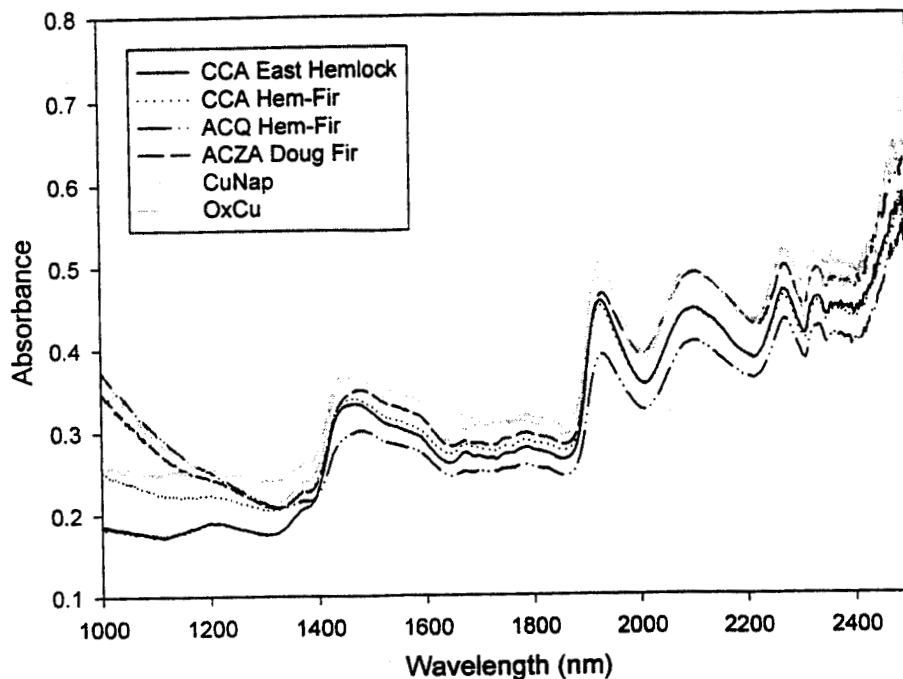


Figure 1. Comparison of near infrared spectra collected from Water-borne and Oil-borne samples.

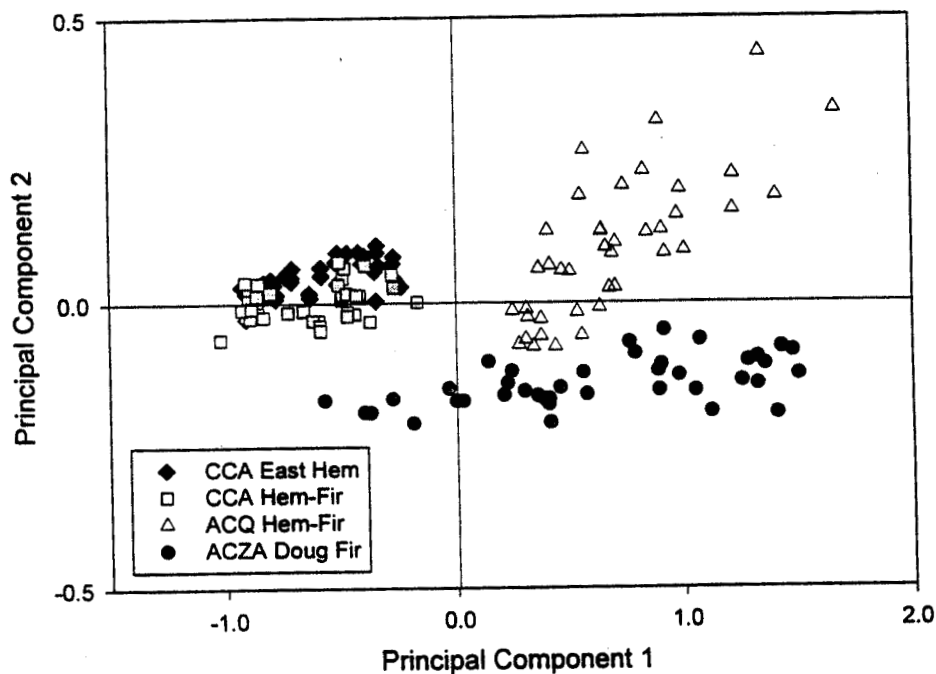


Figure 2. Principal component analysis from NIR spectra collected for Water-borne samples.

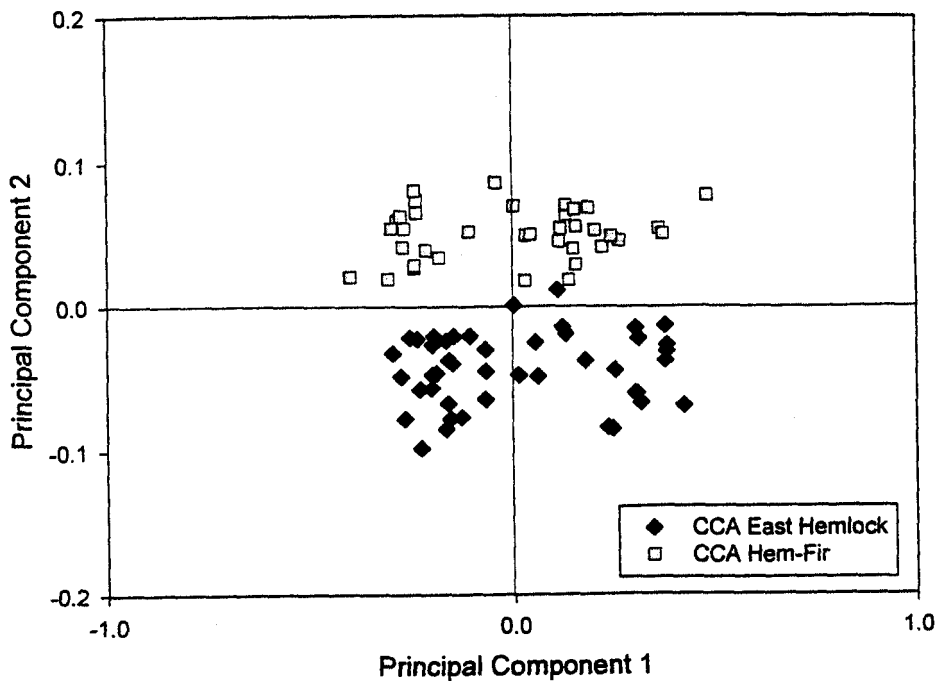


Figure 3. Principal component analysis from NIR spectra collected for CCA samples.

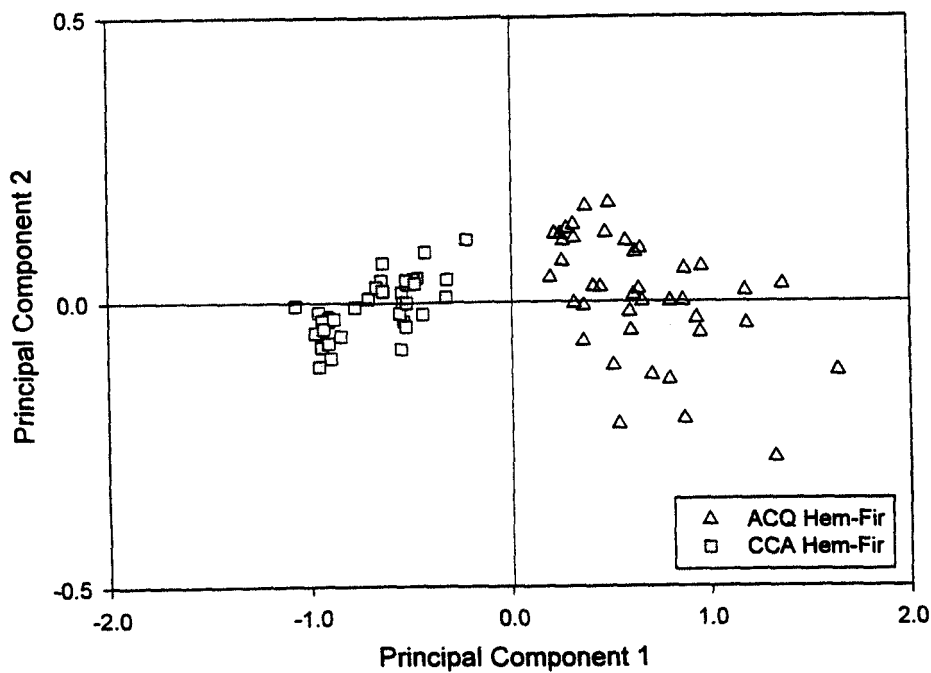


Figure 4. Principal component analysis from NIR spectra collected for Hem-Fir samples.

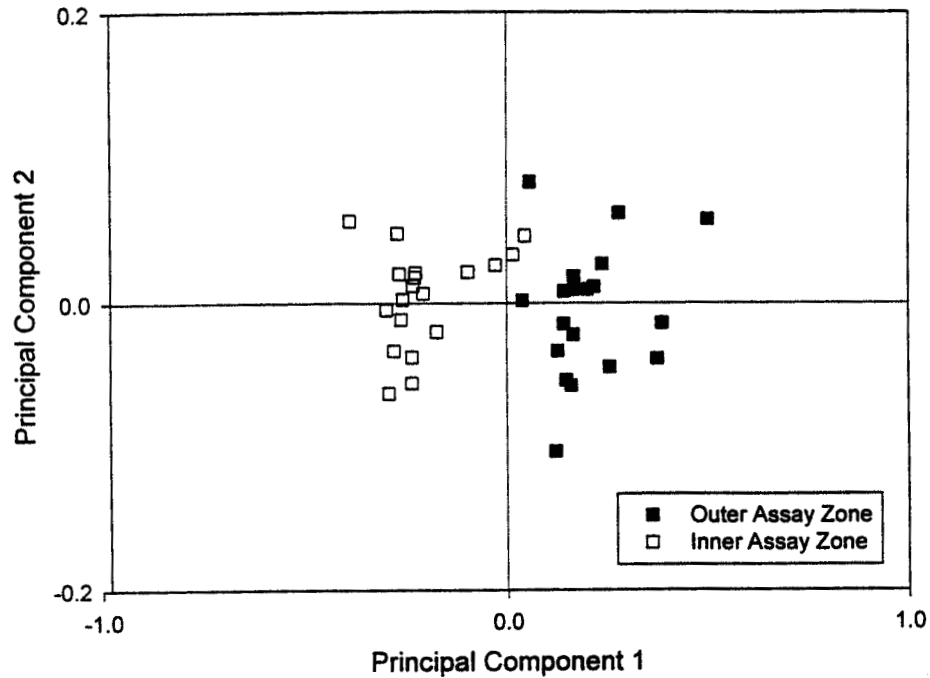


Figure 5. Principal component analysis from NIR spectra collected for CCA Hem-Fir samples.

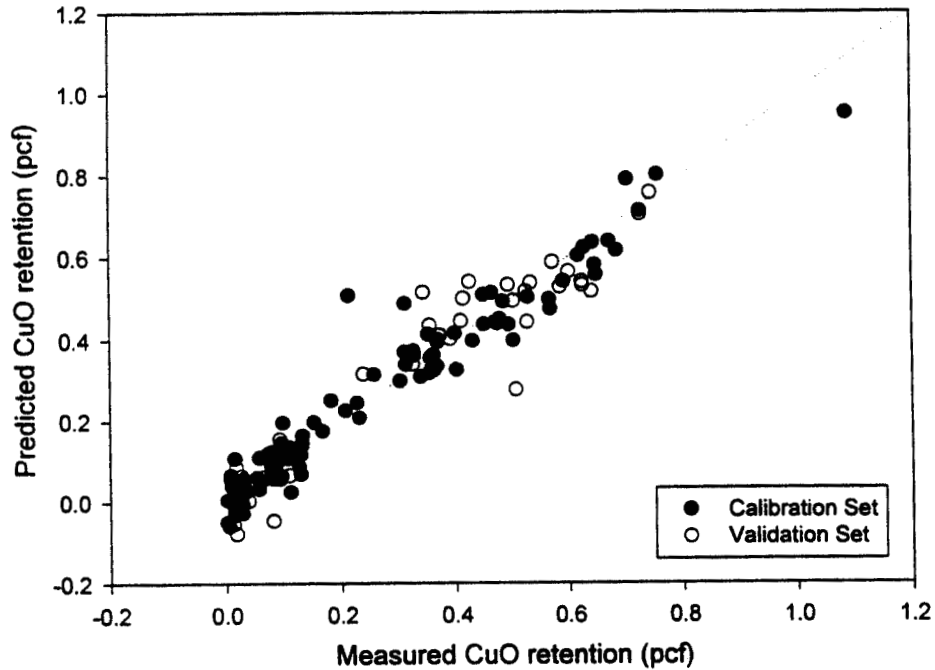


Figure 6. Relationship between measured values of CuO retention and those predicted by PLS-1 modeling using NIR spectra for Water-borne samples.

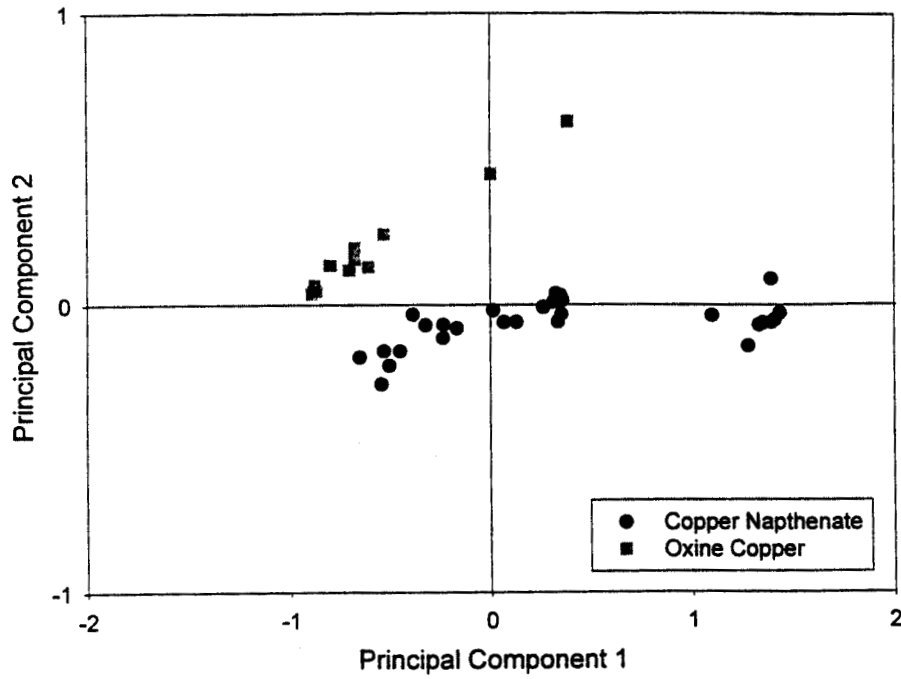


Figure 7. Principal component analysis from NIR spectra collected for Oil-borne samples.

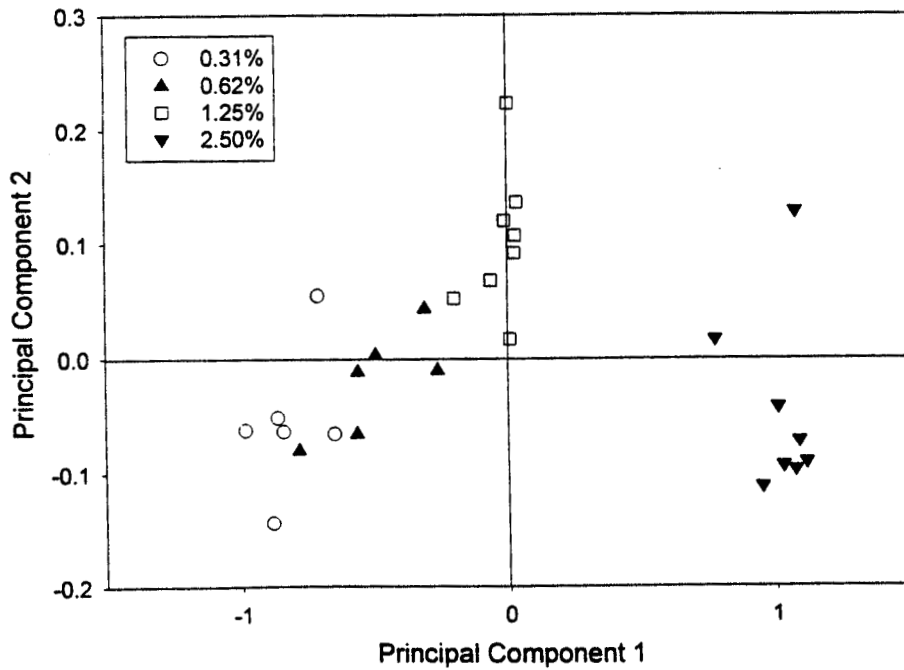


Figure 8. Principal component analysis from NIR spectra collected for Cu Nap samples.

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