

**RAPID ANALYSIS OF METALS IN WOOD PULP BY
DIRECT SAMPLE INSERTION - INDUCTIVELY COUPLED PLASMA
OPTICAL EMISSION SPECTROMETRY**

Michael E. Rybak[#], Panos Hatsis*, Eric D. Salin[#], and Kevin Thurbide*¹

*Pulp and Paper Research Centre and [#]Department of Chemistry,
McGill University, Montréal, Québec, Canada. H3A 2A7

1. Present Address of Corresponding Author:

Department of Chemistry, University of Calgary, 2500 University Drive, N.W.,
Calgary, Alberta. CANADA T2N 1N4 thurbide@ucalgary.ca

ABSTRACT

The analysis of metals in wood pulp is demonstrated using the method of direct sample insertion (DSI) with inductively coupled plasma - optical emission spectrometry (ICP-OES). Using a pyrolytically coated graphite DSI probe, solid wood pulp was directly inserted into an ICP torch, which vaporized the sample and excited the metals present. Prior to plasma ignition and sample insertion, the wood pulp was treated *in-situ* with HCl and NaF, and then dried and ashed by inductively heating the graphite probe in the ICP coil. The total analysis time using DSI was near 5 minutes per sample, as compared to several hours with the conventional acid digestion method currently stipulated in the CPPA and TAPPI standard test procedures. Values obtained for wood pulps analyzed using both DSI and the standard digestion method agree within 2-15% for most metals, and 29-50% for some low concentration elements. The corresponding precision of these values ranged from 7-44% using DSI, compared to 1-40% using the standard digestion method, and was dependant on the pulp sample studied. Results suggest that DSI may be useful for rapidly screening the metal content of wood pulp.

INTRODUCTION

The determination of metals in wood pulp is an important, routine procedure that exists in support of various process and research efforts throughout the pulp and paper industry [1-3]. The current standard method for this analysis, as dictated by both TAPPI and CPPA, involves ashing the sample, dissolving it in hydrochloric acid, and measuring it using solution nebulization into an atomic absorption spectrometer (AAS) [4,5]. Instead of AAS, inductively coupled plasma-optical emission spectrometry (ICP-OES) is now often used because of its multi-elemental capabilities, however the rather lengthy, labour intensive digestion procedure is still commonplace. In order to minimize production delays and ensure product quality, the pulp and

paper industry has a continual need for rapid on-line and off-line monitoring methods [6]. As such, faster methods for obtaining a concentration profile of the metals present in a pulp sample would be beneficial.

In an effort to decrease analysis time and increase sample throughput, the ability to place natural, undigested solids into an ICP has been successfully demonstrated for marine sediments, coal fly ash, and many others using the method of direct sample insertion (DSI) [7-10]. This paper describes the results of analyzing metals in solid wood pulp samples using DSI with ICP-OES.

EXPERIMENTAL

Method Overview

DSI is accomplished by placing the sample into a graphite cup, which is then mechanically elevated into the plasma of an ICP-OES instrument. The probes are made by lathing graphite rods (38 mm x 6 mm i.d.) to form a cup (7 mm depth x 0.25 mm wall thickness) at one end of a stem (16 mm x 2 mm i.d.) and a base (12 mm x 3 mm i.d.) at the other. The base fits to a quartz rod attached to a stepper motor which accurately and reproducibly raises the sample axially into the plasma at specified rates. The sample is then vaporized and signals are collected from the emission of excited metal atoms. The ICP-OES system consists of a Plasma-Therm 27.12 MHz ICP imaged to the entrance slit of a Rowland circle-type polychromator (Model 750, Thermo Jarrell Ash, Franklin, MA, USA) equipped with a galvanically driven background correction system (Trulogic Systems, Mississauga, ON, Canada). These signals, from the time of insertion until the entire sample has been vaporized, are then integrated using a Grams/32 spectral software program (Galactic Industries, Salem, NH, USA). The resulting signal areas are compared to those of external standard solutions, analyzed using the graphite cup in a similar manner, and used to quantify the amount of metal present in the sample.

Samples, standards, and reagents

The wood pulp samples used in this study, a brownstock pulp and a TMP, were provided by the Pulp and Paper Research Institute of Canada (Paprican, Pointe Claire, QC, Canada). These samples were analyzed by Paprican using ICP-OES in the Canadian Pulp and Paper Association (CPPA) standard test method G.34P, and are currently being developed and characterized for usage as industry standard reference materials.

Solutions used for calibration were made by diluting mixed element and single element standards (High Purity Standards, Charleston, SC, USA, and Fisher Scientific, Nepean, ON, Canada) with 0.5% trace metal grade nitric acid (Instra-Analyzed, J.T. Baker, Phillipsburgh, NJ, USA) in distilled, deionized water (Milli-Q water system, Millipore Corp., Bedford, MA, USA). Trace metal grade HCl (Instra-Analyzed) and ACS grade NaF (Baker-Analyzed, J.T. Baker) were used for *in situ* treatment of the pulp samples.

Procedure

About 3 - 5 mg of air dried pulp was accurately weighed into a graphite DSI cup. The cup was mounted on the quartz rod driven by the stepper motor. For specified experiments, 20 μL of HCl and 10 μL of a 10% (m/v) NaF solution were added to the cup at this point. Prior to ignition of the plasma, the cup was positioned at the highest turn of the load coil, and the samples were dried by inductive heating for 2 minutes at 50W forward power (150 $^{\circ}\text{C}$), and then ashed for 2 minutes at 150W forward power (560 $^{\circ}\text{C}$). The probe was then retracted below the ICP coil, the plasma was ignited (2 kW, >2000 $^{\circ}\text{C}$), and the sample was inserted into the plasma for typically 10 - 30 seconds, during which excitation of the elements and signal collection took place. Between runs the cup was reinserted into the plasma to remove any residual material from the analysis. More detailed descriptions of the system can be found in the literature [8,9].

RESULTS

Compared to conventional solution nebulization into an ICP, DSI yields a different type of response with time. The former produces a 'steady state' signal (relatively constant intensity over time) due to the steady introduction of a homogenous metal containing solution. Conversely, DSI generates a 'transient' signal (varying intensity over time) from the excitation of metals as they become vaporized from the solid sample. Due to the different volatilities of the metal species present, DSI conditions, such as plasma forward power and insertion time, must be sufficient to discharge all of the metals from the sample probe.

Initial experiments, using a TMP sample, revealed that insertion of the ashed pulp into a 2.0 kW plasma for 15 seconds was adequate to obtain complete signals from many of the elements investigated (i.e. Mg, Cu, Fe, Mn, Zn). While signals for most of the metals were completed in less than 10 seconds, the iron signals were occasionally longer. When the iron response was too broad it would exceed the signal collection time. This meant that a small portion of the peak would be eliminated from the integration, thus causing errors in the determination of iron.

Broad, tailing signals in DSI-ICP-OES can be improved by various methods. For instance, nonvolatile metallic species, which require more time to vaporize in the plasma, can be converted *in-situ* to volatile metal halides by adding reagents such as HCl and NaF to the sample [7]. As well, sample intercalation into micro-cavities within the graphite surface, which can affect the rate at which metals desorb from the probe, can be offset by pyrolytically coating the graphite cup [8]. Various attempts to alleviate such factors in these experiments were examined by adding NaF and/or HCl to the sample, before or after ashing, using a pyrolytically coated graphite cup. These changes were found to significantly sharpen the signals, and the optimal conditions of adding NaF and HCl prior to ashing the wood pulp were carried throughout the remainder of this study.

Figure 1 illustrates the DSI-ICP-OES signals obtained for different metals from a typical insertion of brownstock pulp under the optimum conditions. As can be seen, all of the signals possess smooth sharp fronts with some degree of tailing on the downward slope. Most analytes were completely vaporized in less than 5 seconds, with extremely volatile elements such as zinc being completely volatilized in 2 seconds. Iron, however, was very difficult to volatilize, with

analyte still being vaporized from the probe 25 seconds after insertion into the plasma. While optimizing the insertion procedure substantially reduced tailing on the iron peak, the volatilization temperature for this element is relatively high compared with the others studied and thus its signal will not be completed as rapidly. In spite of this, it can be estimated from Figure 1 that more than 90% of the iron signal was captured. Incidentally, longer insertion times induced etching on the quartz plasma torch, and so these attempts were discontinued in order to prevent damage to the instrument.

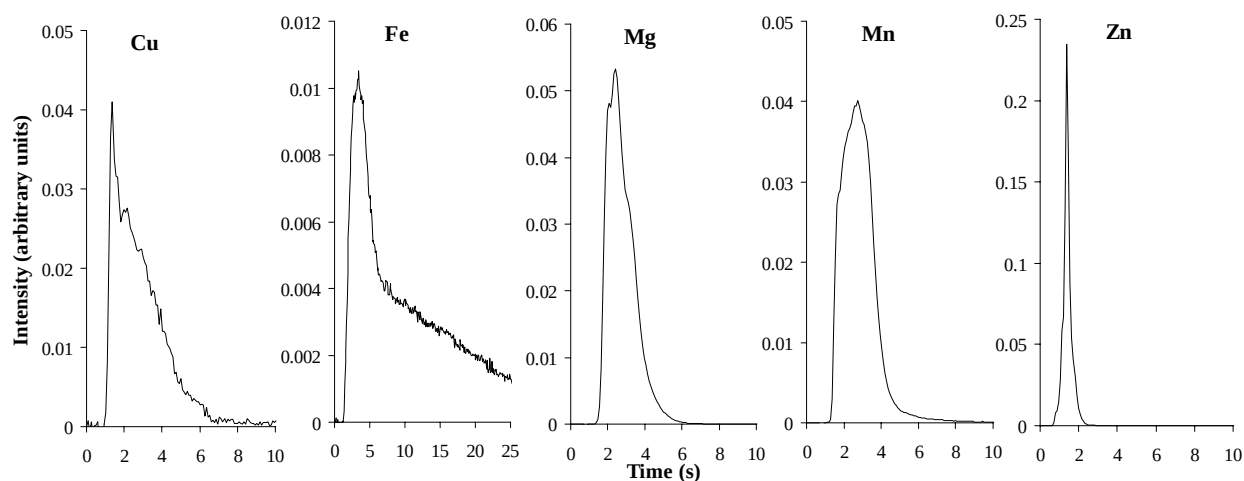


Figure 1. DSI element signals from 3 mg of brownstock pulp. Prior to ashing, 10 μ L of 10% (m/v) NaF and 20 μ L of concentrated HCl were added to the sample in a pyrolytically coated graphite cup used for insertion. See text for details.

Table 1 compares of the concentration of metals present in a brownstock pulp and TMP, as determined using the CPPA standard method G.34P, and DSI. All values reported are based upon external calibration using aqueous standards. Standard additions was also attempted but was not found to perform as well as using external standards. As can be seen in table 1, the values compare reasonably well between the two methods.

The DSI results for the brownstock pulp and TMP generally agree within 2 - 15% of the corresponding values obtained using the standard digestion method. Two exceptions are iron and copper. For each pulp, the DSI method yielded a lower iron value than the standard digestion method, which can be attributed to incomplete volatilization of iron from the sample probe as described earlier (Figure 1). As well for each pulp, the DSI method yielded a larger copper value than did the standard digestion method. The amount of copper in the samples was quite low relative to the other elements determined. At these levels near the detection limit of the standard digestion method, signals can be degraded by noise resulting in quantitation errors. Throughout these experiments, however, DSI consistently demonstrated good sensitivity for copper in wood pulp, yielding signals for this element in many samples that were undetectable using the standard digestion method.

Pulp Sample	Element	<u>CPPA Method G.34P (Paprican) (n=3)</u>		<u>Direct Sample Insertion (n=7)</u>	
		Concentration (ppm)	RSD (%)	Concentration (ppm)	RSD (%)
Brownstock	Mg	515	1.85	593	13
	Zn	11.6	1.80	11.8	20
	Cu	0.84	7.30	1.27	11
	Fe	19.4	12.5	10.7	20
	Mn	80.3	0.99	93.2	6.7
TMP	Mg	212	14.6	201	39
	Zn	14.0	7.73	11.8	16
	Cu	1.10	39.6	1.60	18
	Fe	56.7	1.63	40	44
	Mn	87.7	14.5	91	41

Table 1. Determination of metals in pulp by different methods.

In terms of precision, the standard digestion method almost always produced a lower relative standard deviation (RSD) compared to the DSI method. DSI and the standard digestion method had RSD ranges near 7-20% and 1-13% respectively for the brownstock pulp, and 16-44% and 2-40% respectively for the TMP. With aqueous solutions, DSI commonly demonstrates precision similar to that of solution nebulization, and percentage RSD values of 5% or lower have been achieved [11]. However, with the analysis of solid samples using DSI, other factors such as sample heterogeneity and sample size variability can affect the precision of the technique. The pulp sample weights used for DSI in these experiments are about 10 000 times smaller than those used in the standard digestion method. The pulp samples were received in a granular, air-dried form, some pieces of which were easier to separate and fit into the graphite cup than others. Thus, sampling such small amounts of a largely heterogeneous pulp matrix could contribute significantly to the precision obtained using DSI. The effect of the pulp sample on the RSD of both methods is evidenced by the poorer precision of the TMP analyses relative to the brownstock analyses. To verify the influence of such factors on the RSD in this study, different pulp forms were analyzed using DSI.

Table 2 presents the RSD for replicate metal analyses of four different pulp forms using the DSI method. The different forms investigated were a fresh undried Kraft pulp, a dry fluffed TMP, and a wet TMP sample which was air dried, and then analyzed before and after it was ground slightly. As can be seen, the wet Kraft pulp and dry fluffed TMP samples have a

considerably lower RSD range than does the air dried TMP. This could be related to the clumped, spongy texture that the TMP assumes upon air drying, creating relatively large pieces to sample from, which are more difficult to separate and fit into the graphite cup. Further evidence of this is the fact that, after mild grinding of the same sample for 2 minutes with a mortar and pestle, the RSD values decreased tremendously. The results suggest that the heterogeneity and size of the pulp sample do have a significant effect on the precision of the DSI method.

RSD (%) (n=10)				
Element	Wet Kraft Pulp	Dry Fluffed TMP	Air Dried TMP	
			Unground	Ground
Mg	13	6	32	14
Zn	12	11	123	41
Cu	5	24	97	27
Fe	15	13	48	30
Mn	5	4	119	70

Table 2. Signal reproducibility for different forms of pulp.

Presently, the standard digestion method produces better precision and accuracy than DSI for the analysis of metals in wood pulp. However, the accuracy of the DSI method still measures well, having obtained quantitative results for magnesium, manganese, and zinc, and semi-quantitative results for iron and copper present in the wood pulps. The spread in precision values among both methods illustrates the difficulty in establishing a standard reference pulp, and the 'true' metal content by which different techniques can be assessed. Indeed, the most significant benefit of using DSI is a faster analysis time. Whereas the standard digestion method requires 2-3 hours to complete, DSI requires 5 minutes to prepare and analyze a sample. As well, DSI is fully capable of being automated with a throughput of 30 samples per hour [12]. Considering that typical metal concentrations of industry wood pulp samples can vary over several orders of magnitude, the demonstrated accuracy and precision of DSI-ICP-OES appears more than adequate for use as a rapid screening technique. However, these results are preliminary, and the replicate analysis of more pulp samples with varying concentrations of metals using DSI would be needed to fully characterize this method. Efforts are currently underway to improve the precision and accuracy of wood pulp metals analyses using variations of the DSI concept with larger sample sizes [13].

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