

Heavy metal analysis of inks: a survey

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ABSTRACT *Analytical techniques applicable to the analysis of trace heavy metals in inks are discussed. Results obtained using these techniques by several outside laboratories and by Sun Chemical are presented. A new technique using a microwave oven digestion is presented. The importance of method verification is demonstrated.*

KEYWORDS

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Need for heavy metal analysis in inks

Increasing concern over the environmental impact from solid waste disposed in landfills and incinerators has resulted in a critical examination of the toxicity of all disposable material (1, 2). As a result of this examination, the packaging industry has been asked by various governmental and industrial sources to provide data showing the heavy metal content in its inks. In many states, the Council of NorthEast Governors (CONEG) legislation (3) is the dominant source for heavy metal inquiries. In several states, this legislation requires that packaging components, including inks, contain less than 100 ppm total by weight of the metals Pb, Cd, Hg, and Cr⁶⁺ by Jan. 1, 1994. Within the

graphics industry, another set of metals for which specifications are commonly requested is the CAMALS list. This acronym is composed of the first letter of each of the six metals: cadmium, arsenic, mercury, antimony, lead, and selenium. Other than the seven metals included in CONEG and the CAMALS lists, specifications for as many as 27 other metals might be occasionally requested because they appear on EPA lists, i.e., Pollutant Metals under the Clean Water Act (4)—Al, Ag, As, Au, Ba, Be, Ca, Cd, Cr, Co, Cu, Fe, Hg, Ir, K, Kg, Mn, Mo, Na, Ni, Os, Pb, Pd, Pt, Rh, Ru, Se, Sb, Tl, Sn, Ti, V, and Zn—and Toxicity Characteristics Leaching Procedure (TCLP) Metals (5)—bold-face elements in the list.

Requests for trace heavy metal content have been passed down from consumer product manufacturers through converters to suppliers of

packaging raw materials, particularly ink and pigment manufacturers. Unfortunately, there is no consensus on which analytical method to use for quantifying heavy metals in various ink types.

Analytical methods

There are basically two categories of analytical methods used to determine heavy metal content in inks. The first type measures the acid soluble or leachable metals, the second measures the total metals. If landfill disposal is an issue, then soluble metals is the most commonly requested information; for incineration, total metals content is more relevant.

One of the more frequently used methods for determining soluble heavy metals in inks is the American National Standards Institute (ANSI) Test Z-66.1-1964 (6), which was ex-

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I. Heavy metals analysis of red and blue polyamide laminating inks, ppm^a

Sample	Technique	Ag	As ^b	Ba	Cd ^b	Co	Cr ^b	Cu ^b	Hg ^b	Ni ^b	Pb ^b	Sb ^b	Se ^b	Sr
Blue (neat)	NAA	<2	<12	<10	<37	<1	<3	14000	<2	NA	NA	2.2	<10	<30
	PIXE	<88	<2.6	<21	<106	<3	<3	12300	<8.4	<6	<9	<182	<3.1	<11
	ICP-AES	NA	12	NA	<1	NA	<2	14200	<0.5	1	<2	<2	3.8	NA
	AAS	NA	<5	NA	<1	NA	<5	14500	<0.2	<5	5	<1	<1	NA
Blue (50 ppm spike)	NAA	<2	48	<10	42	<1	50	13000	38	NA	NA	61	33	<30
	PIXE	<98	74	<30	<154	<4	66	17800	48	49	<30	<233	86	<11
	ICP-AES	NA	62	NA	53	NA	53	12700	<0.5	53	56	36	53	NA
	AAS	NA	32	NA	40	NA	46	13600	9	42	21	49	2	NA
Red (neat)	NAA	<1	<6	45	<20	<1	7	<30	<1	NA	NA	2	<4	1000
	PIXE	<8	<0.4	39	<11	0.5	<1	0.9	<1	0.8	<1	32	<0.5	909
	ICP-AES	NA	3	NA	1	NA	0.7	18	<0.5	0.8	0.8	1	<1	NA
	AAS	NA	<5	NA	<1	NA	<5	1	<0.2	5	8	<1	<1	NA
Red (50 ppm spike)	NAA	<2	23	15	<15	<2	31	12	2.9	NA	NA	20	28	1000
	PIXE	<9	32	39	41	<0.5	36	29	6.1	31	<5	85	30	992
	ICP-AES	NA	21	NA	45	NA	72	74	<0.5	69	12	35	44	NA

^aNA = not analyzed.^bNine metals spiked at levels indicated.

panded in the Standard Consumer Safety Specification on Toy Safety, ASTM F 963-86 (7). The intent of the method is to determine the amount of heavy metals a child might ingest from children's toys. These procedures involve heavy metal extraction from ink solids into dilute HCl and quantification using atomic spectroscopy. A similar test, the TCLP, is used for EPA waste characterization. The TCLP is probably the most relevant method of testing for materials ending in a landfill (8). This procedure uses acetic acid extraction of "leachable" metals and quantification by atomic spectroscopy. There are also other methods being used with inks, which involve other types of leaching procedures (5, 9).

Test procedures used to determine total metals content (9, 10) use strong inorganic acids to decompose the organic matrix and release the metals of interest as high boiling soluble inorganic salts. When nitric acid (6 N) with heat is substituted for dilute HCl in ASTM F-963, the procedures are similar to EPA Method 3050 for metal analyses in solids (9). Method 3050 is used for the determination of total heavy metals content.

Methods such as EPA 3050, 3030, and 3040, which are intended for trace heavy metals analysis in soils, waste water, and grease and oils, respectively, are also commonly applied to inks (9). These methods require lengthy digestions and several different elemental analyses using some form of atomic spectroscopy.

II. Method detection limits for heavy metals in liquid inks, ppm^a

Element	PIXE	ICP-AES	GFAAS	NAA
Sb	23	9.0	0.1	1-230
As	0.8	6.0	0.02	5
Ba	6.8	NA ^b	NA	20
Cd	17	1.7	NA	1-150
Cr	2.1	2.1	0.02	5
Cu	0.8	10.1	NA	1-30
Pb	2.5	4.8	0.05	5
Hg	2.5	1.2 (CVAAS)	NA	1
Ni	0.8	2.3	NA	6
Se	0.8	8.4	NA	10

^aAverage for all types of ink tested.^bNA = not analyzed.

There are also ASTM methods for the analysis of low levels of heavy metals in paints which may be applicable to inks (10). In general, these methods are specific for the type of sample and as to the elements quantified. The detection limits are often above 100 ppm or unspecified.

Analytical instruments and techniques

There is a wide range of instrumental techniques which can be used to quantify trace metals in inks. A significant difference exists among the techniques in the requirements for sample preparation. These techniques may be loosely divided into two categories based upon the physical state

requirements for a sample to be introduced into the instrument. The first category (Group I) specifies instruments which can accept virtually any liquid or solid sample. For the second category (Group II), samples must generally be introduced as homogeneous, low viscosity liquids. The first group includes X-ray fluorescence (XRF), proton induced X-ray emission (PIXE), and neutron activation analysis (NAA), all of which are multielemental techniques. Group II includes flame atomic absorption spectroscopy (FAAS), graphite furnace AAS (GFAAS), cold vapor AAS (CVAAS), and inductively coupled plasma-atomic emission spectroscopy (ICP-AES). Of these, only ICP-AES is a multielemental technique.

In Group I techniques, the sample is irradiated using X-rays (XRF), protons (PIXE), or neutrons (NAA). With XRF and PIXE, quantification is made by measurement of the X-ray emission, whereas with NAA, gamma radiation is measured. Depending upon the technique, the irradiation from the element being quantified is measured either immediately (XRF and PIXE) or after given intervals which can be days or even weeks (NAA).

Sample preparation for Group I techniques can be as simple as placing the "as received sample" directly into the instrument. This minimal amount of sample preparation offers significant advantages by: (a) eliminating the potential loss of metals during digestion, (b) reducing analyst time, and (c) allowing for fast turnaround time. These advantages might be very useful in the heavy metal analysis of printed substrates and other packaging materials.

Accurate quantification with XRF or PIXE requires some consideration for sample matrix effects (11). Some of the wide variations in fillers and pigments between various inks can result in substantial changes in X-ray emission levels. This will change both the response factors for a given concentration of a particular element as well as the detection limits.

The various Group II atomic spectroscopic techniques use different methods for atomizing the metals of interest. For example, FAAS uses acetylene/air and acetylene/nitrous oxide burners, ICP-AES uses an argon plasma, GFAAS uses an electrically heated furnace, and CVAAS relies on the high vapor pressure of the element of interest, Hg. Quantification is done by comparison of the atomic emission or absorbance of the metals in the samples to those in standards.

These various techniques have different sensitivities toward specific elements. A convenient and sensitive technique for rapidly analyzing a large number of elements is ICP-AES. GFAAS is generally more sensitive though less convenient. CVAAS is needed for accurate and sensitive quantitation of Hg. Often laboratories perform a combination of the available techniques to obtain the desired detection limits. The primary advantage of the Group II over Group I techniques

is that they can achieve lower detection limits for all heavy metals. In addition, the instrumentation needed is more generally available.

When using Group II techniques, the inks must be prepared to meet the instrument requirements discussed above. This usually necessitates "breaking" down the ink matrix by oxidation of the organic material using heat and concentrated mineral acid in a "wet digestion," followed by filtration to remove any solids. Some disadvantages with this method are the labor involved and potential losses of volatile elements such as Hg, Se, and As during open-vessel wet-digestion. Elements may also be lost during filtration of any insoluble material. Recently, microwave wet digestion of samples in sealed vessels has been successfully used to reduce losses of volatile elements (12).

Method verification

Verification of method accuracy is important in order to establish quality control of these analyses. This is especially true given the recovery problems associated with trace metals analyses. EPA verification procedures involving percent recoveries of spiked samples and determination of detection limits are good examples of acceptable quality control. Part of this report will cover work investigating the accuracy of various trace metal methods according to EPA protocols (9). There is, however, no EPA recommended procedure specifically for determining total trace heavy metals in inks and printed material.

Sun Chemical/P & G joint research project

A joint project was established between Sun Chemical Corp., Packaging Inks (which at that time was BASF Corp., Packaging Inks), and the Procter and Gamble Co., Paper Products Division to evaluate the quality of the ink trace metal analyses. The goals were: (a) to evaluate different analytical (especially multielemental) methods, including those used by outside laboratories; and (b) to establish a reliable trace metal analysis for the three major types of packaging inks—polyamide, nitrocellulose, and aqueous acrylic resin-based inks. An important criterion

established was that any acceptable method should be capable of quantifying the six CAMALS metals at a combined total level of 100 ppm.

Experimental

Open vessel digestion

One gram of ink was placed in a 125 mL Phillips beaker. This was placed on a hot plate with a surface temperature of about 95°C. After evaporation of the solvent, 10 mL of concentrated HNO₃ was added. This was then placed back on the hot plate with the surface temperature at 100°C. Additional nitric acid was added to keep the volume between 5 and 10 mL. Heating was continued until no further digestion appeared to be taking place (usually about 1 h). The samples were then diluted, filtered, and analyzed, as was done with the microwave digested samples.

Microwave digestion

All inks were digested using either a CEM Model 81D or a Floyd RMS-15 OPCM microwave oven. The sample preparation consisted of very slowly adding 10 mL of concentrated nitric acid to a Teflon® vessel containing 1 g of ink. When the vigorous oxidation of the ink and release of nitrogen oxides subsided, the vessel was sealed and heated for 30 min at five different steps of increasing microwave power. After the samples had cooled, they were diluted, filtered, and analyzed. Based on the solubilities of the heavy metal nitrates, it was assumed that losses would not occur during the filtration step. The quantification was done using a Perkin Elmer Model 6000 sequential inductively coupled plasma-atomic emission spectrometer for all elements except Hg. A Perkin Elmer cold vapor atomic absorption spectrometer (CVAAS) was used for Hg measurements. A Perkin Elmer Model 500 graphite furnace AAS was used for analysis of sub-part per million levels of heavy metals in some of the samples.

Ink samples representative of each of three different types of packaging inks were analyzed both neat and spiked at approximately 50 ppm levels. The spiked inks were analyzed to determine percent recovery, accuracy, precision, and detection limits in a manner consistent with EPA guidelines for trace metals (9).

III. PIXE analysis of red and blue aqueous inks, ppm

Sample	Spike ^a	As	Cd	Cr	Cu	Hg	Ni	Pb ^a	Sb	Se
Red	Neat	<1.0	15.0	<2.0	2.0	<2.5	2.4	<2.7	<25.0	<0.9
	10	7.3	18.0	8.6	10.2	12.6	11.0	<5.6	<28.0	8.8
	20	15.4	27.0	16.9	15.3	21.0	19.8	<5.9	<28.0	16.2
	40	28.5	31.6	30.0	26.9	37.1	35.8	<7.0	33.1	34.9
	100	71.6	95.5	93.2	58.4	102.2	88.3	17.7	102.0	76.1
Blue	Neat	<1.0	10.5	<3.3	25.4	<3.1	1.6	<3.5	<34.0	<1.0
	10	7.0	16.4	5.3	30.6	7.0	9.3	<7.0	<30.0	8.3
	20	13.7	23.4	13.3	35.5	21.7	17.4	<5.9	<30.0	15.3
	40	26.6	37.0	32.9	44.5	40.4	33.2	7.6	50.6	31.1
	100	68.1	104.0	82.6	76.8	99.7	80.8	14.3	84.6	68.5
Precision ^b , %		2.2	19	45	3.2	13	1.7	NA ^c	42	5.5
Avg. accuracy ^d , %		69	61	78	59	90	82	68	85	80

^aAll Pb spikes are 25% of indicated levels.
^bRelative standard deviation of 5 replicates of the 40-ppm spiked red ink.
^cNA = not analyzed
^dAvg. accuracy = $\frac{\sum \text{Accuracy for spiked samples}}{\text{Number of spiked samples}}$
 where:
 Accuracy for spiked samples = $100\% - |100\% - \% \text{Recovery}|$
 $\% \text{Recovery} = \frac{C_s - C_n}{C_{ss}} \times 100\%$
 C_s = Concentration determined in spiked sample
 C_n = Concentration determined in neat sample
 C_{ss} = Concentration spiked into sample

Spiking the inks

The spiked inks were prepared using standards made by Inorganic Ventures, Lakewood, NJ. The mixed element standards contained 0.25–1% levels of nine elements: As, Cr, Cd, Cu, Hg, Ni, Pb, Sb, and Se in each of two solvents: 10% HCl and light mineral oil. The spiked inks were shaken for 15 min on a paint shaker. This spiking was done by blending a mixed element standard into the ink prior to sampling. This allowed for determination of factors such as accuracy, precision, and detection limits for the entire method. It more truly represented the test performance on actual inks than spiking procedures calling for spikes after sampling and either before or after wet-digestion.

Results**Survey of analytical techniques**

Samples of a red and a blue polyamide laminating ink were sent to several outside laboratories. Each sample was sent neat and spiked at 50 ppm in each of nine heavy metals, with the exception that Pb was only 12.5 ppm (Table I). The instrumental techniques surveyed were: NAA, PIXE, AAS, ICP-AES. All analyses were performed for total metals content. The objective of

this survey was to evaluate the accuracy of various analytical techniques and to determine the most practical and effective way to quantify trace metals in all types of inks.

Heavy metals in inks using Group I techniques (PIXE, NAA)

The major problem encountered with PIXE was the varying detection limits (Table I and Table II). This was due, at least in part, to matrix effects. For example, the Cd and Sb detection limits were much higher in the blue ink containing percent levels of copper phthalocyanine blue pigment, 154 and 233 ppm, respectively, than in the red laminating ink (Table I). The reason for these high detection limits was the high level of Cu X-ray emission interfering with the weaker emission lines for trace levels of Cd and Sb. In the red ink which was free of Cu, the Sb and Cd detection limits were as low as 11 ppm. These wide fluctuations in PIXE sensitivity indicated that obtaining sufficient detection limits could be a major obstacle to using this technique for testing a wide range of inks, even for only the four elements required by CONEG legislation (3).

The amount and type of interfering elements can vary widely with the

many types of inks. Problems with interfering X-ray emission could be a larger problem on printed material, particularly paper, than encountered with wet inks. This is because of the large Ca, Si, Mg, Al, and other X-ray emission peaks from clays and other fillers present at percent levels on the paper surface.

These matrix problems not only affect the detection limits, but also the accuracy (Table I and Table III). The various matrix effects of different ink formulas upon the X-ray emission efficiency must be evaluated before assuming that accurate quantification is possible. Accurate quantification may require matrix-matched standards for each type of ink. It might be very difficult, however, to prepare a single standard or even a group of standards that are adequately matrix-matched for all possible inks.

A study was conducted to further evaluate the accuracy of PIXE (Table III) with aqueous inks. Two inks were each spiked at concentrations ranging from 20 ppm to 100 ppm (5–25 ppm for Pb) in nine heavy metals. The average accuracy of four spikes in two inks for nine elements was 75%. Generally, the results by PIXE indicate acceptable accuracy, even for EPA specification. These results were

IV. Atomic spectroscopic^a interlab study of spiked laminating inks^{b,c} (percent recovery)^d

Metal	Open vessel digestion				Microwave digestion			
	Lab 1	Lab 2	Lab 3	Sun Chemical	Lab 3	Sun Chemical ^e		
	PA	PA	PA	PA	PA	PA	N/C	AQ
As	73	29	130	85	NA ^f	111	158	59
Cr	NA	28	138	98	180	144	152	149
Cd	119	18	113	99	162	120	130	125
Hg	<4	0	75	NA	NA	62	74	132
Ni	NA	27	116	100	165	99	104	101
Pb	16	15	141	121	180	115	89	13
Sb	82	14	110	36	103	72	98	98
Se	<12	15	65	54	NA	169	160	135

^aLab 1: All metals determined using ICP-AES except Hg using CVAAS.
 Lab 2: All metals determined using ICP-AES.
 Lab 3: Cr, Cd, Ni, Pb, and Sb determined using ICP-AES; Hg using CVAAS; As and Se using GFAAS.
^bPA = polyamide resin based ink.
 N/C = nitrocellulose resin based ink.
 AQ = aqueous acrylic resin based ink.
^cInks were spiked at 20 to 50 ppm.
^dPercent recovery determined as indicated in Table III.
^eResults shown are the average of 5 replicates of three types of ink.
^fNA = not analyzed.

not generated using matrix matching standards, which suggests that such steps might not be required. The limitation with PIXE was the high detection limits of Sb and Cd in some matrices.

While PIXE is an excellent screening technique for detecting heavy metals in inks, it is questionable whether it is applicable for a complete analysis of all heavy metals in all ink matrices at levels approaching 10 ppm per metal. Nevertheless, printed samples and various packaging materials might be best analyzed using this technique. Though XRF was not tested, its similarity to PIXE suggests that similar advantages and disadvantages would be encountered.

Neutron activation analysis (NAA) cannot be used to quantify Pb at levels below several percent because of its very weak gamma emission upon neutron radiation. Ni also shows weak gamma ray emission and cannot be quantified at ppm levels in the presence of higher levels of other metals such as Cu or Sr. These metals are present in many of our inks such as those submitted for NAA to the outside laboratory (Table I). Therefore, this technique is unacceptable for a complete analysis of most of the trace metal specification lists, such as

CONEG (3). In the study, NAA failed to detect 50 ppm Cd and Hg in the red laminating ink (Table I). These spiked values were near the instrumental detection limits for NAA. The recoveries for the other spiked metals were also low in the red ink.

In addition, NAA requires a nuclear reactor as a neutron source and the analysis time is days to weeks. Overall, this technique was not well suited for trace metal analysis of wet inks.

Heavy metals in inks using Group II techniques (ICP-AES, CVAAS, GFAAS)

Open vessel digestion of polyamide resin-based inks. Spiked polyamide resin-based ink samples were digested using nitric acid and analyzed using atomic spectroscopy (Table IV). The recoveries ranged from 0% to 141%. Results from labs No. 1 and No. 2 yielded poor recoveries for nearly all metals. The recoveries obtained by lab No. 3 and by Sun Chemical using the same procedures were better, but still showed some low results for Se and Sb. There are two steps in this procedure which are prone to loss of mercury and other volatile metals (such as As, Se, and Sb): solvent drying and open beaker digestion. The analytical method used by the outside labs involved heating the inks at 95°C to

dryness. This may be a source of the metal losses.

Along with poor recoveries, high detection limits are also a concern when performing an open vessel digestion. Typical dilution factors by this procedure are about 50. This results in ICP-AES (CVAAS for Hg) detection limits for the original wet ink that range from 1 ppm to 10 ppm for each of 10 metals (Table II). It is possible to achieve lower detection limits with atomic spectroscopic techniques in several ways: (a) increase the sample size, (b) concentrate the final solution, or (c) change the sample introduction technique with methods such as GFAAS. All these possibilities have inherent cost and time advantages.

Quantification of the metals in the digested samples can be accomplished using one of several atomic spectroscopic techniques. The most convenient method of analyzing multiple samples is ICP-AES, which is capable of multiple elemental analysis either simultaneously or in a rapid sequential program. FAAS is less sensitive than ICP-AES and requires a separate spectroscopic analysis for each element. Thirteen of the 14 elements specified by various sources can be accurately determined by ICP-AES.

V. Metals content of three packaging ink types—microwave digestion, ppm^a

<i>Ink type</i>	<i>Color^b</i>	<i>As</i>	<i>Ba</i>	<i>Cd</i>	<i>Cr</i>	<i>Cu</i>	<i>Ni</i>	<i>Pb</i>	<i>Sb</i>	<i>Se</i>	<i>Hg</i>	<i>Total^c (CAMALS)</i>
Polyamide	White	<6	1.2	<2	<2	0.5	<2.3	<5	<9	<9	<0.1	<31.1
	Black (1)	<9	NA ^d	<2	<4	0.5	<4.0	<6	<9	<9	<0.1	<33.1
	Black (2)	<6	182	<2	<2	<10	<2.3	<5	<9	<9	<0.1	<31.1
	Yellow (1)	<9	0.9	<2	<4	<10	<4	<6	<9	<9	<0.1	<35.1
	Yellow (2)	<6	NA	<2	<2	<10	<2.3	<5	<9	<9	<0.1	<31.1
	Blue-A (1)	<9	NA	<2	14	>700	4.4	58	<9	<9	<0.1	<85.1
	Blue-A (2)	<9	NA	<2	14	>700	4.8	59	<9	<9	<0.1	<86.1
	Blue-A (3)	<9	NA	<2	14	>700	4.4	54	<9	<9	<0.1	<81.1
	Blue-B	<9	NA	<2	<4	>630	<4	<6	<9	<9	<0.1	<33.1
Nitro-cellulose	Green	<9	NA	<2	<4	>700	17	<6	<9	<9	<0.1	<33.1
	Black	<6	1.2	<2	<2	212	<2.3	<5	<9	<9	<0.1	<31.1
	Blue	<6	2.1	<2	3.2	670	6.1	<5	<9	<9	<0.1	<31.1
	Red	<6	239	<2	<2	6.0	2.3	<5	<9	<9	<0.1	<31.1
	Yellow	<6	>300	<2	<2	NA	<2.3	<5	<9	<9	<0.1	<31.1
Aqueous	White	5	41.0	<2	<2	NA	<2.3	<5	<9	<9	<0.1	<30.5
	White	13.7	3.2	<2	<2	NA	<2.3	NA	<9	<9	<0.1	<38.8
	Black	12.1	2.4	<2	<2	NA	<2.3	NA	<9	<9	<0.1	<34.4
	Blue-A	<6	NA	<2	8.9	>700	76.2	NA	<9	<9	<0.1	<31.1
	Red	10.9	150	<2	<2	1.7	2.3	NA	<9	<9	<0.1	<36.0
	Yellow	<6	0.9	<2	<2	3.5	<2.3	NA	<9	<9	<0.1	<31.1
	Blue-B (1)	<6	1.0	<2	5.8	>700	8.2	NA	<9	<9	<0.1	<31.1
	Blue-B (2)	5.6	0.9	<2	4.0	>700	10.7	NA	<9	<9	<0.1	<35.1
Clay		<6	10.5	<2	<2	00.25	<2.3	<5	<9	<9	<0.1	<31.1

^aAll metals determined using ICP-AES except Hg using CVASS.^bBatch number indicated in parentheses.^cCalculated by adding value of CAMALS metals (boldface symbols) found or detection limit (less than value).^dNA = not analyzed.

VI. Trace metal analysis of sump inks—microwave digestion, ppm

<i>Polyamide ink sample</i>	<i>Time^a, h</i>	<i>As ICP-AES</i>	<i>As GFAAS</i>	<i>Cr ICP-AES</i>	<i>Cr GFAAS</i>	<i>Pb ICP-AES</i>	<i>Pb GFAAS</i>	<i>Sb ICP-AES</i>	<i>Sb GFAAS</i>
Virgin Blue A ^b		<9	0.03	14	12.5	57	45	<9	0.29
Blue A	0	<9	0.05	<3.8	0.69	<6	4.6	<9	<0.1
	13	<9	NA ^c	<3.8	0.87	<6	NA	<9	NA
	24	<9	NA	<3.8	0.92	<6	NA	<9	NA
	63	<9	NA	<3.8	1.17	<6	3.8	<9	<0.1
Blue B	0	<9	0.02	<3.8	0.17	<6	0.66	<9	<0.1
	63	<9	NA	<3.8	0.19	<6	1.26	<9	<0.1

^aTime in sump with press running.^bComplete ICP-AES results for Virgin Blue A and B inks are shown in Table V.^cNA = not analyzed.

Mercury ICP-AES analysis is prone to various problems, e.g., low sensitivity and memory effects. Mercury is best analyzed using CVAAS. The poor recoveries reported for Hg (Table IV) may have been due to either loss during wet digestion (Labs 1 and 2) or the use of ICP-AES at levels near the detection limits (Lab 2).

For most elements, the sensitivity can be increased by using GFAAS in place of ICP-AES. Using GFAAS for As and Se analysis following open vessel digestion, Lab 3 obtained better recoveries for these metals than the other labs. This method, however, could substantially increase the labor required to analyze a large number of samples. The sensitivity of ICP-AES is currently sufficient to meet all of the proposed detection limit requirements.

The lengthy sample preparation time and random inaccuracy exhibited by some labs with the open vessel digestion indicated a need for an improved method. Rather than improve the open vessel digestion, a microwave digestion was developed.

Microwave digestion. There are some significant advantages in using a microwave oven with closed vessels for digestions (12). The higher temperatures and pressures which build from the acid vapors, solvent, and decomposition of the organic matrix in the closed Teflon vessels allow for a fairly quick digestion of the ink matrix. The closed vessels are only opened after the digested sample has cooled to ambient temperature, which greatly reduces losses of volatile metallic species. In addition, the microwave digestion does not require constant attention. Typical research grade microwave ovens have carousels that hold 12 digestion vessels which are rated to withstand 1400 kPa (200 psi).

Spiked polyamide, nitrocellulose, and aqueous acrylic-based ink samples were digested using a microwave oven. The method used in this study required 30 min as compared to the typical 2 h or more of open vessel digestion required on a hot plate. Overall, the sample preparation time using a microwave oven is reduced by at least a factor of 2. Another advantage of the ink microwave digestion was that the dilution factors, hence the detection limits, were approximately

half those from the open vessel digestion.

Quantification of the heavy metals was performed in the same manner as used for open vessel digested samples, i.e., ICP-AES and CVAAS. The percent recoveries using microwave digestion obtained by Sun Chemical for the three different kinds of inks ranged from 59 to 169 (Table IV). This range does not include the 13% recovery for Pb in the aqueous ink. The reason for this unusually low value for only aqueous acrylic resin inks has not been determined.

Outside lab No. 3 using the same microwave digestion procedures achieved recoveries ranging from 103% to 180% (Table IV) for the polyamide resin-based inks. Surprisingly, this lab's results were better using open vessel digestion. Using microwave digestion, problems still exist (at both Sun Chemical and Lab 3) with high percent recoveries and occasionally with low recoveries even though a yttrium internal standard was used at Sun Chemical. Internal standards are commonly used with ICP-AES analyses to reduce matrix effects resulting from incompletely digested organic compounds and dissolved solids that affect sample transport rate (13).

High recoveries that cannot be eliminated by using an internal standard suggest that the matrix is affecting the plasma in such a way that the emission responses for the various metals are affected to different degrees. These residual matrix effects can be reduced by more thorough digestion or by dilution of the final solution. Alternatively, they can be accounted for by standard additions. These techniques, which were not investigated, will affect the analysis time or the sensitivity of the method.

Analysis of three types of packaging inks. After determining the percent recoveries for the microwave digestion of the three major types of packaging inks, the method was used to quantify trace heavy metals in several inks of each type. The results (Table V) showed that most inks contained less than 10 ppm of each of the CAMALS metals. The typical total value of the six CAMALS metals ranged from 30 ppm to 39 ppm. Three

batches of the polyamide blue ink ranged from 81 ppm to 86 ppm.

Heavy metal concentrations of inks collected on an operating press. The possible buildup of heavy metals in inks during a press trial was evaluated. This was done on inks being used in a flexographic press printing on polyethylene (Table VI). In order to determine the heavy metal concentrations which were below the detection limits of ICP-AES, As, Cr, Pb, and Sb were analyzed by GFAAS.

In this study, two different blue inks were sampled from the virgin inks received by the converter and from the sumps of a single press at intervals over a 63 h test period. One of the inks, Blue A, contained 50 ppm Pb in the virgin ink and lower levels of Cr and Ni. These concentrations were diluted below the ICP-AES detection limits when made press ready and sampled from the sump. No buildup of heavy metals was detected throughout the 63-h test period.

Summary

These results demonstrated that all techniques for determination of heavy metals in inks have limitations and that no set of data from a single technique or laboratory was without some problems. PIXE may be useful in surveying for heavy metals, but care must be taken in accounting for matrix effects when high levels of interfering elements are present. ICP-AES (CVAAS for Hg), following microwave digestion, is capable of quantifying most heavy metals in most inks.

Even with considerable attention to sample preparation, the accuracy of these methods is lower than typically attained during analysis of wastewater and soil samples (5, 6). This is not surprising in view of how much more complex inks are than typical wastewater and soil samples. The authors believe that the accuracy of the method can best be improved by assuring a more thorough microwave digestion.

Analysis of several inks, which were formulated not to contain any heavy metals, has generally shown concentrations below the detection limits of ICP-AES and CVAAS. Extensive work to accurately quantify elements

which are below these detection limits is probably unnecessary.

The percent recoveries reported in this work indicate that Group II techniques can screen reliably for the presence of all heavy metals presently listed on all of the various government lists (6-9). If a particular element is detected at a high enough level to cause a batch of ink to be outside of specification limits, more extensive work would be warranted. For the majority of inks, which easily meet heavy metal specifications, normal procedures described herein are sufficient.

As demonstrated in the interlaboratory survey, it is important that all laboratories perform ink spiking percent recovery studies to verify their procedures. The percent recovery studies must be performed on ink samples spiked prior to digestion. In any analysis, recoveries and detection limits should be established for each different type of ink. This is the best means to recognize these problems and establish adequate quality assurance. □

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