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Determination of Trace Metals in Marine Paints

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There are numerous applications of paints (pigments) in marine environments. Organic and inorganic pigments are commonly used in marine paints. Inorganic pigments are generally salts of iron, titanium, lead, cadmium, chromium, zinc, and aluminum (Ash and Ash 1978; Boxall and Von Fraunhofer 1977; Turner 1980). Therefore, there is potential threat of metal pollution from the use of paints in marine environments.

In one environmental research project of Saudi Aramco, the world largest oil company, we were confronted with the problem of trace metal determination in the paints commonly used in the Arabian Gulf. An on-line search revealed limited analytical information on metal determination in marine paints. Rastogi (1992) determined four metals in finger and make-up paints. He mixed water-based paints with nitric acid and the mixture was fluxed for three hours at 180°C. The filtrate was used for metal determination. The grease paints of cosmetic significance were extracted in hexane, and substituted to by nitric acid digestion as in the case of water-based paints. In a special publication, ASTM (1972) suggested procedures for determining major metallic components in paints (such as, Al, Fe, Pb, Cu, Mo, Cr, and Zn). The objective of this research was to compare different sample preparation procedures as applied to analyzing paints for determining trace metals.

MATERIALS AND METHODS

Marine paints samples were provided by the Environmental Affairs Division of Saudi Aramco. A brief description of these samples is given in Table 1. Three sample preparation techniques were used to determine trace metal concentrations in these paint samples. These sample preparation procedures are listed below.

Dry Ashing: Each paint sample was blended thoroughly using a thick glass rod.

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Immediately after blending, quadruplicate samples of 1 to 2 g of homogenized paint sample was placed in 50-mL crucibles. Each crucible was charred on very low heat on a hot plate, cooled, and transferred to a furnace. The furnace was slowly heated to 500°C. Ashing of the paint samples in the crucibles was conducted overnight (for about 14 hours). On cooling, six mL of aqua regia was added to each crucible. The contents were digested to near-dryness on a hot plate to convert metal oxides to their respective chlorides. The aqua regia digestion procedure was repeated, and then the residue was dissolved in 5 mL of concentrated double-distilled HNO_3. About 15 mL of distilled water was added to each crucible. The aliquot was filtered using Whatman filter paper # 42, and the volume was increased to 50 mL . This solution was used for metal determination using an inductively coupled argon plasma analyzer (ICAP).

Nitric/Perchloric Acid Digestion Procedure: Quadruplicate samples of about one gram of thoroughly homogenized paint sample was placed in 80-mL beakers. Each beaker was heated slowly on a hot plate to char the content. Ten mL of concentrated ultrapure HNO_3 and 5 mL of $HClO_4$ were added to each beaker. The content was heated to white $HClO_4$ fumes and near dryness. Another 5 mL of concentrated HNO_3 and 2 mL of $HClO_4$ were added, and the digestion procedure was repeated. Then 5 mL HNO_3 was added, and the content was heated to dissolved residues. About 10 mL of distilled water was added to each beaker, the aliquot was filtered using Whatman # 42 filter paper, and the filtrate volume was increased to 50 mL. Metal concentrations were determined in these acid digest samples.

Nitric/Sulfuric Acid Digestion Procedure. This procedure was similar to that of the above except that H_2SO_4 was used in place of HNO_3, and HNO_3 acid in place of $HClO_4$.

Two paint samples (A-1260 and A-1271) were randomly chosen for recovery study. Each paint sample was prepared in two sets of five replicates following each of the above procedures. One set of paint samples was spiked with Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, V, and Zn standard solutions to give one ug/mL of final volume. The other set was used as control or baseline for calculating recoveries. These samples were prepared and analyzed as described above.

Metal concentrations were determined in each paint sample using an ICAP. Each sample was read five times for 10 seconds each, and an average of these determinations were computed along with standard deviation. If the standard deviation was found to be more than 10%, the determinations were either repeated or discarded. Reagent blanks were also prepared and analyzed as that of paint samples. Metal concentrations in the reagent blank samples were subtracted from the metal concentrations in the paints. All chemicals used in this study were of highest purity, except for H_2SO_4, which was of ACS grade. Average recoveries of spiked metals in paint samples A-1260 and A-1271 are given in Table 2.

Table 1. A brief description of paint samples used in this study.

Sample ID	Name of Sample and Comments
A-1259	Hempadur-4517-1791, high solids polyamine cured epoxy paint base with marine applications
A-1260	Hempathane Top-Coat 5521-4098, aliphatic polyurethane coating base with excellent gloss and wide application
A-1261	Hempadur Hi-Build-4520-1148, polyamide cured high build epoxy paint base with applications in marine environments.
A-1262	Hemples Coal tar Epoxy-mastic-3565A-1999, high solids, high build polyamide cured coal tar epoxy base coating with excellent resistant to seawater and crude oils.
A-1263	Tropalin Aluminum -5253-1900, alkyd based aluminum pigment paint
A-1264	Hempadur Zinc-1536-1984, zinc rich polyamide cured epoxy primer.
A-1265	Hemples Silicone Aluminum 5691-1900, heat resistant aluminum pigmented paint.
A-1266	Hemples Zinc Chromate-Primer-1205SA-222, zinc chromate primer based on long oil alkyd
A-1268	Hempadur Primer-1530-2178, epoxy primer base containing zinc phosphate as corrosion inhibitor
A-1269	Hempalin non-skid Deck Paint 5337-1148, styrenated alaked paint containing an anti-slip aggregate, largely used in marine environments
A-1270	Hempadur Hi-Build-4523-143, like A-1261, it is a polyamide cured high build epoxy paint base with applications in marine environments
A-1271	Hemples Silicone Aluminum 5694-1900, it is a heat resistant, acrylic modified silicone aluminum pigmented paint base
A-1272	Hempadur 4515-1987, high solids polyamine cured epoxy paint base with marine applications
A-1273	Hemples Galvosil 8571-1984, solvent borne, self curing inorganic zinc silicate coating, largely used as rust preventing primer
A-1274	Hemples Galvosil 1578-1984, same as Hemples Galvosil 8571-1984
A-1275	Hemples Enamel White-5214-1000, alkyd enamel with good gloss weather resistance properties and applications in marine environments
A-1267	C/A-9545, curing agent for 4515, polyamine used as a curing agent for epoxy based paints
A-1276	C/A 9574, curing agent for 1536, polyamine used as a curing agent for epoxy based paints
A-1277	C/A 957SA, curing agent for 356SA, polyamine used as a curing agent for epoxy based paints

Table 1. Contd.

Sample ID	Name of Sample and Comments
A-1278	C/A 9504, curing agent for 1530, polyamine used as a curing agent for cross-linked epoxy based paints
A-1279	C/A 9504, curing agent for 4523, polyamine used as a curing agent for epoxy based coatings
A-1280	C/A 9537, curing agent for 5521, used for curing aliphatic polyurethane bases
A-1281	C/A 9504, curing agent for 4520, polyamine used as a curing agent for epoxy based coatings
A-1282	C/A 9540, Curing Agent for 4517, polyamine used as a curing agent for epoxy based paints

Table 2. Recoveries (%) of spiked metals in different sample preparation procedures.

Metal	Dry Ashing		Nitric/Perchloric		Nitric/Sulfuric	
	Mean*	STD	Mean	STD	Mean	STD
Barium	81.9	5.2	88.9	4.6	-	-
Cadmium	84.7	7.4	90.1	3.4	86.0	4.5
Cobalt	88.3	6.5	89.3	8.9	90.0	5.7
Chromium	87.3	4.8	86.3	6.4	-	-
Copper	85.1	7.9	88.1	3.1	73.4	18.7
Manganese	86.4	3.2	88.5	3.7	85.3	8.5
Nickel	89.3	2.4	90.4	5.6	86.5	8.8
Lead	71.5	23.5	93.5	5.0	114.5	11.2
Vanadium	79.7	8.3	93.1	6.5	89.7	9.0
Zinc	97.9	3.2	88.9	7.7	83.3	10.3

* Mean of recoveries of five replicates

STD Standard deviation of mean

RESULTS AND DISCUSSION

Concentrations of metals found in the marine paint samples are listed in Table 3. Barium recoveries in the dry ashing and nitric/perchloric acid procedures were above 80%. Understandably, Ba recoveries were very poor (<40% and are not listed in Table 2) in nitric/sulfuric acid combination due to the formation of insoluble barium sulfate. This can also be seen in Table 3, where, for example, Ba concentrations reduced significantly in nitric/sulfuric acid treated samples. Sample preparation procedures seem to have no effect on Cd recoveries which were above 85% (Table 2). In general, there was a good agreement in Cd concentrations between all sample preparation procedures (Table 3). Recoveries of Co was similar to that of Cd.

Table 3. Metal concentrations in different paint samples. All values are in mg/kg except given otherwise.

Sample ID	D.A.	N.P.	N.S.	D.A.	N.P.	N.S.
		Barium			Cadmium	
A-1259B	3.1	1.4	0.9	7.8	8.1	7.7
A-1260B	16.4	15.1	bdl.	3.6	2.7	3.9
A-1261B	66.0	62.5	3.3	1.0	0.9	2.6
A-1262B	80.8	76.6	2.6	1.5	1.3	2.0
A-1263B	2.7	0.5	bdl.	8.3	8.8	6.1
A-1264B	2.3	2.9	2.1	31.9	39.7	35.9
A-1265B	1.9	1.8	0.4	9.3	11.4	10.5
A-1266B	199.	204.	3.3	20.3	21.1	21.3
A-1267B	56.9	54.0	5.1	0.5	0.7	bdl.
A-1268B	42.5	41.0	17.9	16.4	20.0	17.3
A-1269B	6.9	8.0	4.1	1.1	0.6	0.8
A-1270B	7.3	6.8	3.5	2.3	2.4	4.7
A-1271B	bdl.	bdl.	0.7	11.8	13.8	11.6
A-1272B	10.0	18.3	8.2	9.8	7.5	9.5
A-1273B	3.7	3.8	2.8	bdl.	0.5	0.1
A-1274B	0.3	0.5	0.9	bdl.	1.2	1.3
A-1275A	1.7	bdl.	bdl.	bdl.	bdl.	1.6
A-1276B	bdl.	0.1	bdl.	bdl.	0.1	bdl.
A-1277B	bdl.	0.1	bdl.	0.4	0.1	0.6
A-1278B	bdl.	bdl.	bdl.	bdl.	bdl.	bdl.
A-1279B	bdl.	bdl.	bdl.	bdl.	bdl.	bdl.
A-1280B	bdl.	bdl.	bdl.	bdl.	bdl.	bdl.
A-1281B	1.5	bdl.	bdl.	0.1	bdl.	bdl.
A-1282B	44.3	53.0	3.1	0.8	bdl.	bdl.
		Cobalt			Chromium	
A-1259A	3.6	1.4	1.4	258	270	274
A-1261B	1.0	1.3	1.6	22.3	21.9	20.7
A-1262B	1.7	1.8	1.2	2.7	0.4	0.7
A-1263B	151	158	141	8.9	9.7	5.9
A-1264B	6.8	8.9	7.8	1.6	1.9	1.4
A-1265B	1.5	1.9	1.1	3.5	4.4	2.6
A-1266B	117	127	115	bdl.	8.30%	8.36%
A-1267B	0.8	1.2	0.3	5.8	8.2	8.9
A-1268B	3.7	4.8	3.7	20.8	20.0	11.2
A-1269B	305	288	253	20.1	17.0	19.6
A-1270B	0.6	1.0	0.9	7.7	8.0	3.7
A-1271B	1.7	2.4	3.4	3.0	14.4	0.9
A-1272B	1.6	1.6	4.3	3.7	4.9	4.2
A-1273D	bdl.	0.5	0.5	bdl.	0.7	0.8
A-1274D	bdl.	0.3	1.7	bdl.	0.3	0.2
A-1275B	215	220	235	bdl.	0.8	0.7

Table 3. Contd.

Sample ID	D.A.	N.P.	N.S.	D.A.	N.P.	N.S.
	Cobalt	Chromium				
A-1276B	bdl.	bdl.	0.7	bdl.	0.1	bdl.
A-1277B	bdl.	bdl.	0.8	bdl.	0.1	0.3
A-1278B	bdl.	0.5	0.4	bdl.	0.1	bdl.
A-1279B	bdl.	bdl.	0.3	bdl.	0.6	0.2
A-1280B	bdl.	bdl.	0.3	bdl.	0.1	0.4
A-1281B	bdl.	bdl.	0.2	bdl.	0.5	0.1
A-1282B	0.1	0.2	0.2	bdl.	0.7	0.6
		Copper			Manganese	
A-1259B	9.5	7.0	9.1	49.1	30.3	45.6
A-1260B	89.9	86.0	65.9	7.3	6.5	6.4
A-1261B	4.6	6.6	3.4	180	170	166
A-1262B	1.4	bdl.	0.9	238	225	202
A-1263B	9.2	bdl.	5.6	16.6	17.6	12.2
A-1264B	bdl.	0.9	bdl.	2.1	2.5	2.3
A-1265B	5.1	5.5	3.3	8.3	8.8	8.1
A-1266B	1.1	3.8	bdl.	19.9	20.9	17.8
A-1267B	1.0	1.3	bdl.	148.	151.	122.
A-1268B	bdl.	0.6	bdl.	123.	127.	117.
A-1269B	11.8	10.2	3.9	2.9	2.7	1.7
A-1270B	2.3	1.2	bdl.	8.5	10.2	8.1
A-1271B	4.8	5.7	0.9	10.2	11.5	9.0
A-1272B	6.2	7.9	5.5	38.6	66.0	37.6
A-1273D	0.4	2.5	bdl.	1.4	1.6	bdl.
A-1274D	bdl.	1.3	bdl.	bdl.	0.4	bdl.
A-1275B	1.9	3.0	bdl.	bdl.	bdl.	bdl.
A-1276B	1.0	1.7	bdl.	bdl.	0.3	bdl.
A-1277B	0.3	1.1	bdl.	bdl.	0.1	bdl.
A-1278B	0.7	1.3	bdl.	bdl.	0.2	bdl.
A-1279A	0.3	0.6	bdl.	bdl.	0.1	bdl.
A-1280B	1.2	1.1	bdl.	bdl.	0.1	bdl.
A-1281B	0.3	1.4	bdl.	bdl.	0.3	bdl.
A-1282B	3.8	4.4	2.5	5.1	10.4	6.0
		Nickel			Lead	
A-1259B	37.9	36.8	35.8	12.0	9.8	7.5
A-1260B	11.3	10.3	9.2	0.61%	0.58%	433.
A-1261B	2.2	2.2	3.2	126.	122.	54.4
A-1262B	3.5	3.1	3.1	24.5	27.3	11.7
A-1263B	6.3	6.5	4.2	209	227	145
A-1264B	21.9	32.9	30.9	274	348	307
A-1265B	4.5	5.8	4.9	255	319	267
A-1266B	16.7	19.2	21.6	1275	1379	709
A-1267B	1.2	2.1	1.3	5.6	8.1	4.5

Table 3. Contd.

Sample ID	D.A.	N.P.	N.S.	D.A.	N.P.	N.S.
		Nickel			Lead	
A-1268B	11.0	12.9	10.2	63.5	69.8	52.1
A-1269B	5.3	4.4	4.0	7.6	7.2	6.9
A-1270B	2.7	2.8	3.3	39.8	37.1	33.7
A-1271B	6.4	8.0	8.6	315	380	303
A-1272B	5.5	4.3	9.3	257	192	204
A-1273D	bdl.	1.3	1.0	bdl.	4.1	4.0
A-1274D	bdl.	0.7	0.3	bdl.	2.1	9.6
A-1275B	2.3	2.1	3.9	65.2	58.6	66.1
A-1276B	bdl.	1.1	2.2	bdl.	1.0	3.6
A-1277B	bdl.	0.3	0.4	bdl.	0.6	5.1
A-1278B	bdl.	0.2	bdl.	bdl.	0.3	bdl.
A-1279A	bdl.	0.3	bdl.	bdl.	0.7	bdl.
A-1280B	bdl.	bdl.	bdl.	bdl.	bdl.	bdl.
A-1281B	bdl.	0.9	bdl.	bdl.	0.3	bdl.
A-1282B	bdl.	bdl.	bdl.	20.4	12.5	13.1
		Vanadium			Zinc	
A-1259B	4.8	3.7	5.7	319	89.6	79.3
A-1260B	1.4	2.9	4.0	389	113	113
A-1261B	1.8	2.9	6.2	758	53	53.0
A-1262B	3.1	3.1	3.9	723	463	319
A-1263B	6.0	6.9	4.5	81.6	34.6	13.4
A-1264B	bdl.	bdl.	bdl.	67.02%	60.7%	59.8%
A-1265B	5.3	6.1	6.1	24.4	144.6	97.0
A-1266B	14.5	17.4	16.4	3.45%	3.98%	3.44%
A-1267B	bdl.	bdl.	bdl.	16.4	28.6	25.9
A-1268B	4.6	5.2	4.6	2.83%	2.27%	2.20%
A-1269B	bdl.	bdl.	bdl.	35.3	51.7	27.8
A-1270B	5.1	4.1	10.9	7.7	17.2	7.9
A-1271B	4.7	10.4	9.8	25.3	68.2	19.1
A-1272B	4.0	3.8	8.2	25.1	29.0	17.9
A-1273D	bdl.	0.9	bdl.	7.3	17.4	14.6
A-1274D	bdl.	0.2	bdl.	3.8	4.7	4.1
A-1275B	bdl.	bdl.	bdl.	245	247	217
A-1277B	bdl.	bdl.	bdl.	bdl.	2.7	1.1
A-1278B	bdl.	bdl.	bdl.	bdl.	2.1	3.4
A-1279A	bdl.	bdl.	bdl.	bdl.	2.0	6.7
A-1280B	bdl.	bdl.	bdl.	5.8	2.0	8.1
A-1281B	bdl.	bdl.	bdl.	3.7	8.0	6.5
A-1282B	bdl.	bdl.	bdl.	16.7	36.3	24.6

D.A. Dry ashing procedure N.P. Wet digestion with nitric/perchloric
N.S. Wet digestion with nitric/sulfuric bdl. Below detection limit of ICAP

Chromium recoveries were found to be >86% in dry ashing and nitric/perchloric treatment but no data were collected for nitric/sulfuric acid combination. It seems that nitric/sulfuric acid treatment evaluated Cr concentrations in paints, especially in samples of curing agents. This may be due to contamination of sulfuric acid by this element. Recoveries of Cu in nitric/sulfuric treatment was the lowest and highly variable. This is supported by the analytical data in Table 3. These variations may be attributed to residual metal content of sulfuric acid and probable precipitation of copper sulfate during sample preparation. Recoveries and concentrations of Mn in the paint samples were not significantly affected by the samples preparation procedures.

Nickel recoveries were statistically similar and were >86% in all the sample treatments. These observations are also supported by the data in Table 3. Recovery of spike Pb was highly variable, especially in dry ashing treatment. It varies between 71.5 to 114.5%. It seems that Pb was lost during dry ashing procedure and enhanced due to contamination of sulfuric acid (high reagent blank) in the samples prepared by nitric/sulfuric acid combination. The data on Pb concentrations in the paint, pigment, and curing agent samples were also significantly variable ($p < 0.05$). It seems from the data that nitric/perchloric acid combination is the most suitable for determining Pb in paint samples.

Relatively low recoveries of V were found in dry ashed samples suggesting its loss during sample preparation. Vanadium recoveries were statistically ($p < 0.05$) similar in the wet digested samples. The analytical data in Table 3 support these general observations. The maximum Zn recoveries were found in the dry ashed samples. Similar trend can be seen in the analytical data in Table 3.

From the foregoing, it may be concluded that sample preparation procedures have not affected recoveries and concentrations of Cd, Co, Mn, and Ni in paint samples. Concentrations and recoveries of Ba and Cu were the lowest, but Pb and Cr recoveries and concentrations were enhanced in nitric/sulfuric acid combination. Dry ashing procedure reduced concentrations and recoveries of Pb and V. The maximum recoveries of Zn were found in samples that were dry ashed. In general, metal concentrations followed trends exhibited by their recovery study.

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