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Examination of Paints by Trace Element Analysis

The examination of paint in this laboratory and many others is done, essentially, by two techniques. These are microscopy, for the physical characteristics and layer structure, and pyrolysis gas chromatography (PGC), for the resin type. X-ray diffraction is often used as an additional examination for establishing the nature of pigment and is effective in routine cases, particularly those involving automobile paint of varied colors. Microscopy, however, is of limited value in cases involving white and black paints, whereas PGC is less effective than microscopy in dealing with household paints, most of which contain alkyd-type resins. The X-ray diffraction pattern of household paints generally shows only titanium dioxide (TiO_2) pigment and is of limited value. For the examination of white paints, therefore, we require an effective technique for differentiation. Analysis of the large number of trace elements contained in paint has been shown to be a useful technique in the discrimination of paints [*1*].

This project was aimed at discriminating white household paints by analysis of trace elements through neutron activation analysis (NAA).

Experimental

Neutron Activation Analysis

The irradiations were done for 4 h at 5 MW in the nuclear reactor at McMaster University, Hamilton, Ontario, Canada. The counting was done using a 4096-channel pulse height analyzer connected to a Ge(Li) detector. The data were collected on punched paper tape and processed by a Sigma 3 computer to locate peaks and their areas. The elements were identified from their gamma ray energies and half-lives. The concentrations were calculated using standard samples.

Household Paints

White household paint samples in liquid form were obtained from major manufacturers and were prepared by dipping a clean glass slide into each and air-drying the slides. Samples (less than 10 mg) were scraped off these slides for our experiments. At least duplicate samples were analyzed in each case.

Results and Discussion

The analysis showed the presence of the following elements: ytterbium, molybdenum, titanium, lutetium, mercury, chromium, gold, zinc, tungsten, copper, arsenic, antimony,

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gallium, silver, iron, manganese, cadmium, and sodium. Generally the (n,γ) reaction was used. Under the conditions of our work, where the reactor is about 40 miles (64 km) away, short-lived nuclides cannot be measured. Among the above elements only Ti produces a short-lived (n,γ) product. However, it produces ^{47}Sc as a result of ^{47}Ti (n,p)^{47}Sc reaction which is long lived and gives a gamma ray peak at 155 keV. Titanium analysis was therefore made by measuring the ^{47}Sc produced.

The results are given in Table 1. Nearly half the samples analyzed were alkyd-based, and the pigment was TiO_2 in all of them. The trace element composition of duplicate samples was generally within ±10%. Many of the samples are distinguishable on a qualitative basis. With several samples, however, quantitative data is necessary to distinguish them.

In some cases, some of the trace elements such as Hg, Cr, and Au, are not reproducible. This may be due to sample inhomogeneity or to the concentrations being at the sensitivity limit. Some of these problems can be solved by using larger samples or long irradiation times. In routine case work, it is advisable to analyze at least duplicates of each sample to determine what elements are significant and reproducible.

Neutron activation analysis can be routinely applied to case work. Its advantages are that it requires little of the examiner's time, sample preparation is minimal, and after irradiation is done (which does not require the examiner's time) the samples are counted nearly automatically. By using modern equipment with computer assistance, multi-element quantitative analysis is done with a high degree of automation.

Automobile Paints

A set of 17 white and black paints from panels supplied by the manufacturer were analyzed, and the results are given in Table 2. The samples from different years by the same manufacturer were distinguishable, as were samples from the same year by different manufacturers. Again, both qualitative and quantitative analysis were effective.

Case Applications

Trace analysis by NAA is a useful method for differentiating paint samples, particularly with white and black paints and in those cases where samples are too small to give reasonably good quality pyrograms.

An application of NAA to a specific case involved a hit-and-run accident between two vehicles of almost identical yellow color. The microscopic and pyrolysis GC results were consistent. The gamma spectra are given in Figs. 1 to 4. The quantitative analysis of major peaks is given in Table 3. The major peaks represent significant quantities of the elements where the reproducibility in duplicates is within ±10%. The results are consistent. The overlap of gamma spectra (which is equivalent to qualitative analysis) of control and suspect paints is noteworthy.

Summary

Trace element analysis using neutron activation analysis is effective and valuable, particularly in the examination of white household paint. Although physical appearance and resin composition are generally similar in these paint samples, trace element composition provides an effective way of distinguishing among them.

In the case of automobile paint samples, NAA serves as an important additional technique for discrimination. The technique is important when sample sizes are very small. The technique developed takes a few minutes for sample preparation, a few hours of irradiation time (during which the examiner's presence is not required), and

TABLE 1—*Neutron activation analysis of white household paints (measured in counts per minute for each milligram of sample).*

Sample	Yb	Mo	Ti	Lu	Hg	Cr	Au	Zn	W	Cu	As	Sb	Ga	Ag	Fe	Mn	Cd	Na
								Manufacturer No. 1										
1	...	...	2483	227	...	...	...	966	...	489	208	286	130	90	90	1696	...	1 384
2	...	163	3205	...	...	...	66	769	64	153	...	...	57	...	...	...	57	1 332
3	542	438	2307	405	291	315	278	635	256	612	554	...	...	188	189	1663	...	5 446
4	781	...	2479	...	173	...	...	440	...	214	...	...	...	...	...	...	...	2 819
5	1137	...	3678	...	...	...	175	...	...	485	...	...	...	...	...	...	151	543
6	289	...	1391	...	...	...	340	...	58	...	...	...	...	...	...	990	...	688
7	...	...	1809	659	...	...	...	...	...	2629	...	...	...	...	...	4419	...	5 849
8	...	...	1857	...	...	410	...	...	...	...	...	357	...	...	...	6628	...	4 157
9	...	...	1590	...	...	...	...	19 488	...	2080	...	...	...	...	...	819	...	740
10	...	...	1802	...	...	...	290	770	...	...	...	...	263	232	...	...	...	8 270
11	...	...	1984	...	...	...	...	...	...	452	...	5767	...	...	...	...	294	8 877
12	...	...	1959	...	...	...	...	...	...	...	...	918	622	...	...	640	...	13 782
13	350	...	2413	...	...	...	...	...	...	...	...	...	...	...	...	...	...	1 210
14	1113	...	...	...	...	...	...	...	...	...	...	...	...	...	105	...	...	3 688
15	264	...	234	...	44	...	...	...	...	...	...	...	...	...	...	...	...	174
								Manufacturer No. 2										
16	...	...	2087	...	...	...	...	...	...	...	...	...	...	...	...	...	...	261
17	...	...	1228	46	...	...	...	...	...	...	...	129	...	...	...	...	...	600
18	...	107	1189	...	...	...	...	...	...	...	...	...	...	...	...	...	...	941
19	...	102	483	...	...	...	...	130	...	...	387	...	...	...	...	...	...	347
20	...	...	1340	...	...	...	64	...	...	...	...	...	...	...	...	...	...	105
21	...	...	730	143	128	...	...	...	46	...	...	3150	185	...	...	...	...	468
22	...	...	1565	523	...	...	...	...	...	...	...	...	321	347	...	...	...	9 855
23	...	...	1700	...	...	...	...	84	...	...	...	...	...	...	...	...	...	539
								Manufacturer No. 3										
24	...	1202	2246	...	...	...	...	769	...	...	...	...	...	...	...	6007	...	5 476
25	...	...	1480	1418	...	...	...	31 687	...	3212	...	953	...	...	...	5203	...	4 101
26	...	371	3045	...	254	...	...	1 020	...	377	150	...	...	...	...	...	...	4 277
27	...	276	2365	...	...	...	...	...	...	...	150	...	...	130	...	1206	130	3 202
28	...	...	1486	...	...	213	...	372	...	305	330	...	...	273	...	1131	929	3 609
29	...	1448	1060	...	506	479	...	...	466	765	...	...	...	...	...	...	...	9 960
30	...	...	2359	...	...	...	...	...	...	...	740	...	...	...	...	2257	689	15 854
31	...	...	823	...	622	591	...	...	...	...	...	...	...	...	...	630	...	4 075
32	...	...	1248	...	...	...	...	...	...	...	...	...	...	...	...	...	...	10 826
33	...	...	3143	...	...	...	...	...	...	...	710	...	...	...	381	...	387	9 787

Manufacturer No. 4

34	207	...	538	...	...	...	...	...	...	...	...	...	...	...	...	387	2 119
35	...	...	498	...	...	...	...	176	...	316	...	153	...	...	...	...	5 247
36	...	...	586	...	139	...	95	...	...	...	...	...	...	...	77	...	2 798
37	...	...	917	...	...	...	...	...	...	...	...	...	...	...	...	...	2 337
38	262	...	1316	...	...	...	...	572	83	153	79	138	...	...	...	1414	...	1 319
39	1397	...	867	...	...	...	...	...	...	...	475	...	...	...	...	...	...	11 996
40	1094	875	202	...	...	...	531	...	...	...	...	...	471	...	...	...	...	8 895
41	...	...	1137	...	750	...	...	...	...	...	...	...	...	...	...	1534	...	16 116
42	...	...	454	...	...	...	...	460	...	...	355	...	...	...	...	...	...	3 881
43	...	...	1752	244	...	...	...	...	...	...	...	...	...	...	...	166	...	5 113

TABLE 2—*Neutron activation analysis of automobile paints (concentration in ppm).*

Sample	Source	Color	Cu	Na	Zn	Mn	Ba	Cr	Co	Sb	K	Ti	Br
1	AMC 1971	white	21	188	5038	2.5	7 200	...	...	1.7	232	830	31.3
2	AMC 1972	white	14	204	4788	0.74	...	72	...	1.6	182	742	19.5
3	AMC 1973	white	19	136	4633	0.34	...	...	9.9	...	...	827	...
4	Chrysler 1971	white	13	373	4038	2.7	...	...	...	...	...	697	40.1
5	Chrysler 1972	white	8	255	3785	4.2	3 269	...	...	0.81	604	609	...
6	Chrysler 1973	white	8.4	109	2983	3.4	2 900	...	...	...	...	1596	...
7	Ford 1971	white	26	429	2312	6.4	...	...	...	...	...	1892	52
8	Ford 1973	white	8	725	...	1.7	...	...	11	...	...	823	...
9	GMC Truck 1973	white	7	2.7	...	1.0	...	...	2201	...	...	1615	...
10	GMC 1973	white	8	553	...	1.8	...	...	...	...	...	1683	...
11	GMC 1973	white	...	450	...	1.2	...	...	...	...	...	1564	55
12	AMC 1971	black	95.1	57.1	2978	27.2	97 200	1034	0.55	2.7	400	...	...
13	Chrysler 1971	black	27.2	72.2	...	50.5	...	206	...	...	...	...	88
14	Chrysler 1973	black	7.5	39	...	4.1	703	...	...	...	...	...	56
15	Ford 1971	black	66	58.6	...	17.7	378	...	...	...	...	...	71
16	Ford 1972	black	10	105	...	6.7	5 264	...	...	...	120	...	415
17	GMC 1972	black	210	621	8.2	0.51	...	...	...	...	...	...	...

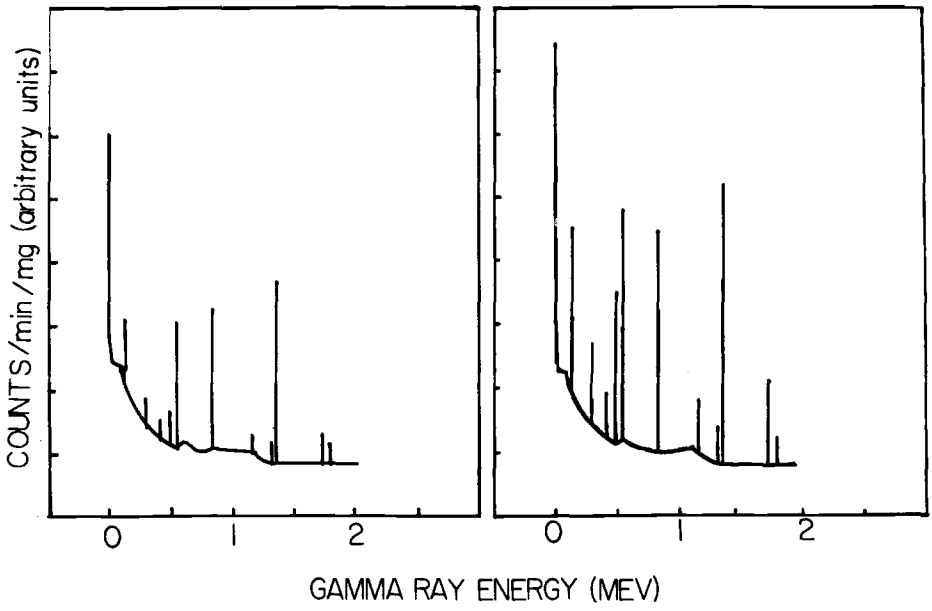

FIG. 1—*Comparison of gamma ray spectra;* (left) *repaint from suspect's vehicle;* (right) *foreign repaint found on suspect's vehicle.*

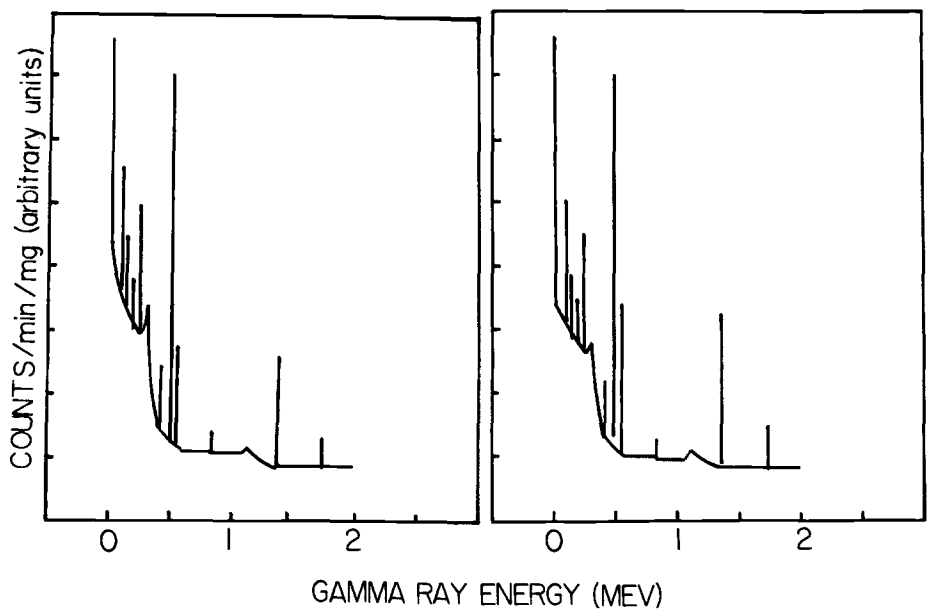

FIG. 2—*Comparison of gamma ray spectra;* (left) *original refinish and primers from complainant's vehicle;* (right) *foreign paint found on suspect's vehicle.*

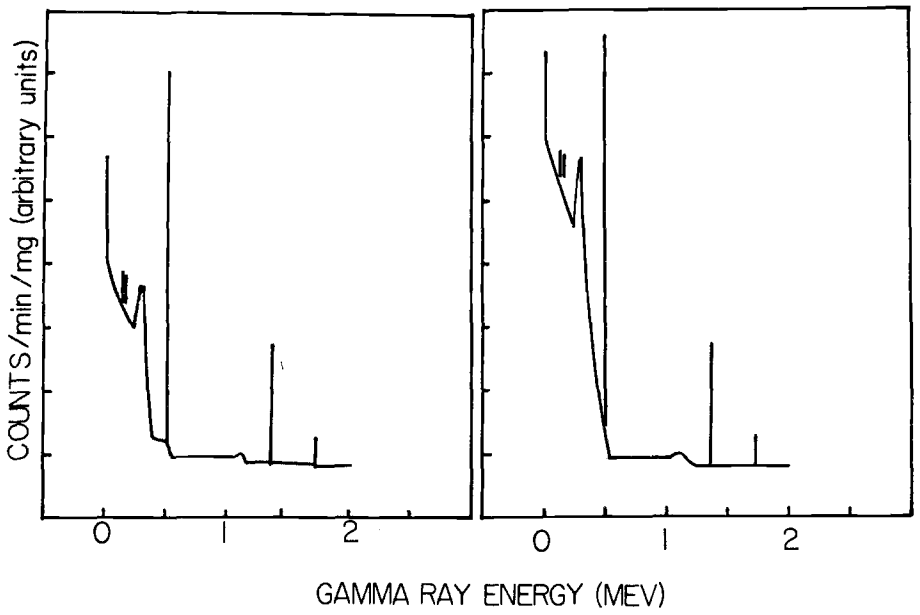

FIG. 3—*Comparison of gamma ray spectra;* (left) *refinish paint from complainant's vehicle;* (right) *foreign repaint found on suspect's vehicle.*

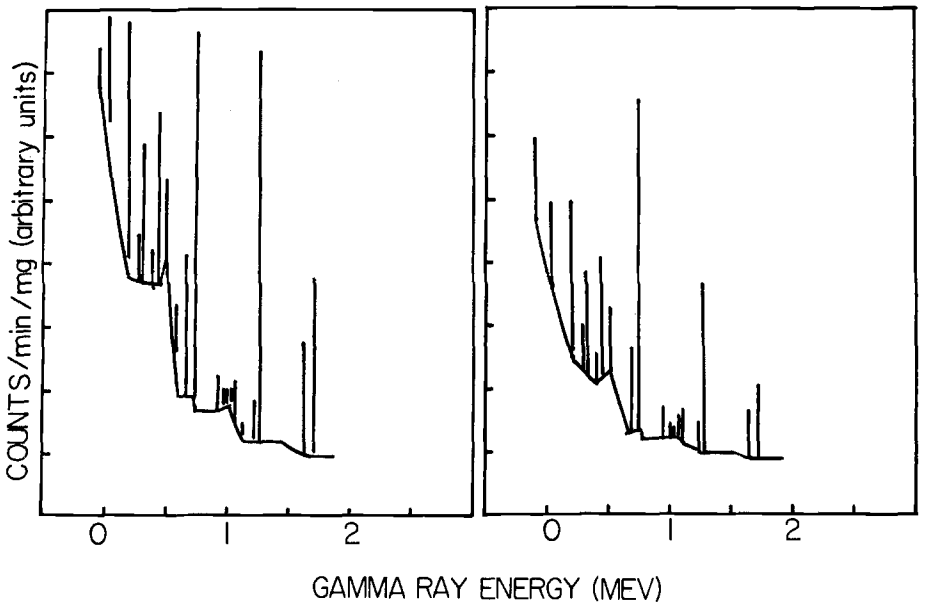

FIG. 4—*Comparison of gamma ray spectra;* (left) *repaint from suspect's vehicle;* (right) *foreign repaint found on complainant's vehicle.*

TABLE 3—*Case application of neutron activation of paints.*

Sample	Source	Mo	Ti	Hg	Cr	Au	Cu	Sb	Mn	Sc	Fe	Co	Na	Zn	As
1	control repaint from from complainant's vehcile	399	755	...	270	...	119	868	1230	...	220	164	1553	...	...
2	foreign repaint on suspect's vehicle	...	646	...	351	384	678	898	838	61	184	167	1490	...	...
3	original refinish and primers from complainant's vehicle	...	1377	...	763	31 834	...	2879	356	...	...	....	1721	...	...
4	found on suspect's vehicle	...	1955	1166	749	27 351	...	3222	412	...	...	...	3749	...	...
5	control refinish from complainant's vehicle	...	2513	...	...	...	72 013	...	...	...	...	...	3972	...	...
6	foreign refinish on suspect's vehicle	...	2979	...	...	2 122	87 020	...	...	...	...	...	2987	...	...
7	control repaint from suspect's vehicle	...	1797	...	1174	...	...	...	7041	...	...	...	1646	692	944
8	foreign repaint found on complainant's vehicle	...	1569	...	1100	...	...	...	5050	...	...	...	1187	730	841

then a few minutes for counting and obtaining quantitative multielement concentration patterns. A technician can easily handle 30 to 50 samples per day.

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[*1*] Erickson, N. E., Krishnan, S. S., and Perkons, A. K., "Present Status of NAA in Forensic Science," Canadian Society of Forensic Science, Annual Meeting, Montreal, Sept. 1965.

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