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Victor Reeve,[1] *B.A. and Thomas Keener,*[1] *B.A.*

Programmed Energy Dispersive X-Ray Analysis of Top Coats of Automotive Paint

Elemental analysis is a necessary approach to the characterization of physical evidence in forensic science laboratories [*1*]. There are many wet chemical and instrumental methods in use; however, with few exceptions, these techniques are difficult to apply, have considerable sample size or preparation constraints, are time consuming, or are destructive. Energy dispersive X-ray (EDX) spectrometry does not have these disadvantages [*2,3*].

The analytical system used in this study is EDX spectrometry in conjunction with a minicomputer capable of sorting numerous emission energies and furnishing output on either a cathode ray tube (CRT) or a teletype. The emission energies displayed on the CRT represent the elemental composition of the material [*3,4*].

The forensic analysis of paint samples generally requires time-consuming analytical techniques. Samples that cannot be differentiated by obvious physical properties should be compared on the basis of their organic and inorganic chemical composition before a final conclusion is reached [*5*]. This study is concerned with the inorganic composition of the paint samples and in particular with a technique that rapidly and nondestructively determines the elemental composition of paint samples for comparisons. Any technique that can do this is invaluable in a forensic science laboratory [*5*,p. 138].

After examining the results of a study [*6*] that compared the ability of emission spectrography and EDX to differentiate automotive paints, the authors decided to develop an automated technique for the EDX analysis of automotive paint samples.

In 1974, the U.S. National Bureau of Standards (NBS) Law Enforcement Standards Laboratory prepared and distributed a standard reference collection of 140 American automotive surface coatings used in 1974 entitled *Automotive Colors* to forensic science laboratories throughout the United States. The paint standards represent those types that were new for the model year or were carried over from previous years. Further information in the collection included sample number, metallic or nonmetallic flaking texture, manufacturer reference number, and automobile make and model using the paint color. All the top coats in this collection were prepared from production line batches sprayed on aluminum or paper sheets. The painted sheets were compared visually and instrumentally against master color standards and then cut into 25 by 40-mm samples. For these reasons it was decided that analytical results from the collection would

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[1] Manager and student aid, respectively, Applications and Training Office, California State Department of Justice, Sacramento, Calif.

interest the forensic science community, and the automated technique developed for EDX was demonstrated by the analysis of these standard paint samples.

The authors determined the elemental composition of these paint samples and tabulated the data (Table 1). Matters outlined include operating conditions, comparison of sample data, evaluation of EDX spectrometer stability, homogeneity of samples, and homogeneity of corresponding paint samples from different NBS *Automotive Colors* collections.

Method

Samples from the NBS collection were analyzed for inorganic components, both qualitatively and semiquantitatively, by using a Finnigan 900F EDX spectrometer. Preliminary work established the optimum conditions for analyzing the paint standards. All the paint samples were prepared for analysis by removing them from their holding frames and placing them on the rotating sample tray in the X-ray cavity.

The instrument conditions used were 31.0 to 35.0 kV and 4.00 mA for the excitation energies of the rhodium X-ray tube with dead time of 35 to 40% on the analog-to-digital converter (ADC). The samples were irradiated in an air path using a rhodium filter and indium collimator. Although bremsstrahlung radiation was increased with these operating conditions the detection of the heavier elements was improved. The indium collimator was used for two reasons: it has an absorption edge higher than most elements detected and the short (1.6-mm) collimator allowed the detector to receive emissions from a broad area of the specimen. If lightweight paint chips (approximately 50 μg) or small areas (approximately 0.25 mm^2) are to be examined, the longer molybdenum collimator has to be used and the samples have to be prealigned with the collimator.

Initial testing disclosed that the paint standards are divided into four main categories defined by the predominant elemental peak: iron, barium, titanium, and lead. Occasionally, a different category was observed (calcium or strontium), but this was infrequent and these exceptions were not separately categorized.

Most of the paint specimens on aluminum sheets exhibited the presence of copper which was attributed to electrolytically deposited copper on the backing between the aluminum sheet and the sprayed paint. The copper deposit was observed visually, and paint samples that were affected are indicated by an asterisk in Table 1. Approximately 75% of the paint samples were mounted on aluminum backings. The backing was sufficiently excited by the X-ray beam to interfere with analysis. A spectrum stripping technique to overcome this problem has been evaluated and is considered in greater detail in a later portion of this study. Those samples with aluminum backing without the electrolytically deposited copper are indicated by two asterisks in Table 1.

Certain elements were common to many of the samples (Table 2). Each sample was analyzed automatically for 12 elements by programming the 16-K core computer of the EDX system. Observation of the areas of selected elemental peaks and differentiation of background counts from peak area counts were performed as indicated in Fig. 1. A total of 512 channels in each half of the memory core retained energy pulses received from the detector. When an element was present, its particular energy pulses were directed to the corresponding channels in the vicinity of the channel defined as the peak centroid (peak ID) (Fig. 1) and the pulses were counted and stored for tabulation and display.

A width of eleven channels was designated in the program, with the center channel superimposed on the peak ID. Five channels spanned each side of the peak ID in a symmetrical fashion. This channel width was sorted and counted, irrespective of peak size, by following routine channel calibration procedures. Right and left spans for defining the background area beneath each peak were established to create as consistent a

TABLE 1—*Elemental composition of automotive paints used in 1974.*[a]

Sample	Metallic Paint	Counting Time, s	Ca	$Ti\text{-}K_\alpha$/$Ba\text{-}L_\alpha$ Ratio	$Ti\text{-}K_\beta$/$Ba\text{-}L_\beta$ Ratio	Cr	Mn	Cu	Zn	$As\text{-}L_\alpha$/$Pb\text{-}L_\alpha$ Ratio	$Se\text{-}K_\alpha$	$As\text{-}L_\beta$/$Br\text{-}K_\alpha$ Ratio	$Pb\text{-}L_\beta$/$Se\text{-}K_\beta$ Ratio	Sr
Iron-Based Paints														
B0051**	yes	67	0.003	0.364	0.068	0.009	0.607	0.305	...	...	...	0.004	0.012	0.018
B0052	yes	144	1.13	0.857	0.148	...	...	...	0.548	...	...	...	...	0.122
B0092*	yes	82	...	0.002	0.003	0.188	0.920	0.546	0.388	...	...	0.033	0.010	0.051
B0129**	yes	77	...	0.007	...	0.292	0.919	0.537	0.256	0.003	...	0.008	0.031	0.044
C0041	no	155	1.12	1.00	0.184	...	...	...	0.567	0.005	...	...	...	1.05
C0080**	yes	74	0.004	0.404	0.056	0.023	0.797	0.431	...	...	...	...	...	0.029
C0090*	no	70	...	...	...	0.136	0.728	0.495	0.178	0.006	...	...	...	0.028
E0068	yes	44	0.238	0.374	0.071	0.021	0.001	...	0.111	...	...	...	...	0.075
E0085**	yes	44	...	0.248	0.037	0.011	0.470	0.224	...	...	...	...	0.031	0.022
E0130*	yes	40	...	...	...	0.070	0.387	0.218	0.023	...	...	...	0.001	0.029
F0009*	yes	23	0.002	0.486	0.404	0.076	0.109	0.057	0.024	0.198	...	0.002	0.142	0.122
F0012*	yes	27	0.008	0.353	0.276	0.069	0.220	0.098	0.005	0.009	...	...	0.002	0.048
F0013**	yes	14	0.004	0.271	0.194	0.034	0.073	0.033	0.009	...	...	...	...	0.061
F0025*	yes	14	...	0.204	0.154	0.027	0.090	0.032	0.020	...	...	...	...	0.051
F0031**	yes	21	0.001	0.430	0.378	0.043	0.110	0.054	0.343	0.017	...	...	0.014	0.188
F0032**	yes	35	...	0.851	0.768	0.112	0.174	0.086	0.746	0.005	...	...	...	0.336
F0038**	yes	19	...	0.444	0.422	0.051	0.072	0.039	0.328	0.006	...	...	...	0.208
F0039**	yes	29	...	0.628	0.546	0.074	0.144	0.096	0.550	0.022	...	0.054	0.009	0.272
F0040**	yes	14	0.006	0.268	0.244	0.033	0.061	0.024	0.270	...	...	...	...	0.128
F0047	yes	30	0.186	0.320	0.048	...	0.005	...	0.078	...	...	0.052	...	0.027
F0059	yes	28	0.157	0.274	0.046	...	0.007	...	0.080	0.005	...	...	...	0.103
F0062	yes	52	0.324	0.555	0.097	...	...	...	...	0.148	...	...	0.016	0.051
F0071	yes	157	1.28	0.960	0.165	...	...	...	0.573	...	...	...	...	0.250
F0074	yes	35	0.241	0.197	0.039	0.006	0.003	...	0.097	0.019	...	...	...	0.019
F0075	yes	65	0.391	0.812	0.136	...	...	...	0.157	...	...	...	0.008	0.092
F0077*	yes	76	...	0.375	0.058	0.020	0.702	0.342	...	0.189	...	...	0.189	...
F0078*	no	21	...	0.456	0.071	0.007	0.159	0.112	...	...	...	...	...	0.038
F0082**	yes	36	...	0.226	0.036	0.009	0.361	0.206	...	0.008	...	0.008	...	0.044
F0084	yes	1559	1.35	0.184	...	...	...	...	0.593	...	...	...	...	0.230
F0089**	yes	56	...	0.143	0.014	0.004	0.512	0.288	0.019	...	...	...	...	0.024
F0109**	yes	27	...	0.396	0.249	0.032	0.169	0.103	0.038	...	...	...	0.008	0.080

TABLE 1—*Continued.*

Sample	Metallic Paint	Counting Time, s	Ca	$Ti-K_\alpha$/ $Ba-L_\alpha$ Ratio	$Ti-K_\beta$/ $Ba-L_\beta$ Ratio	Cr	Mn	Cu	Zn	$As-L_\alpha$/ $Pb-L_\alpha$ Ratio	$Se-K_\alpha$	$As-L_\beta$/ $Br-K_\alpha$ Ratio	$Pb-L_\beta$/ $Se-K_\beta$ Ratio	Sr
F0110*	yes	21	...	...	...	0.067	0.221	0.146	0.042	0.003	...	...	...	...
F0111*	yes	18	...	0.018	...	0.031	0.171	0.093	0.021	...	0.037	0.017	...	...
F0112*	no	37	0.005	0.899	0.145	0.042	0.314	0.196	0.052	...	...	0.014	...	0.033
F0113*	yes	11	...	0.003	...	0.031	0.107	0.049	0.040	...	...	...	...	0.007
F0114*	no	20	...	0.456	0.060	0.038	0.161	0.115	0.022	...	...	...	...	0.014
F0116*	yes	46	0.004	...	...	0.093	0.470	0.337	0.133	...	...	...	...	0.014
F0126*	yes	54	...	0.010	0.004	0.200	0.572	0.342	0.213	...	...	0.151	...	0.026
F0127*	yes	36	...	...	...	0.096	0.386	0.200	0.186	0.007	...	0.017	...	...
F0128*	yes	52	...	0.003	...	0.170	0.542	0.416	0.069	...	...	...	...	...
F0133*	yes	11	...	...	...	0.021	0.096	0.066	0.016	0.012	...	...	0.002	0.004
F0134*	yes	55	0.003	0.004	...	0.061	0.417	0.276	0.095	...	...	0.019	0.029	0.012
F0137*	yes	21	0.001	0.003	0.004	0.087	0.230	0.121	0.051	...	...	...	0.005	0.010
F0138*	yes	10	0.004	0.005	0.006	0.018	0.102	0.044	0.015	...	...	...	...	...
F0139*	yes	55	...	...	...	0.160	0.612	0.401	0.073	...	...	...	...	0.035
G0088**	yes	20	...	0.064	0.011	0.004	0.180	0.192	0.014	...	...	...	0.012	...
H0036*	no	27	...	0.911	0.370	0.036	0.165	0.074	0.042	...	0.004	...	0.008	0.079
H0048*	yes	55	...	0.382	0.059	0.016	0.482	0.241	...	...	...	0.011	...	0.046
H0066*	no	19	...	0.405	0.068	0.001	0.172	0.116	...	...	...	...	0.021	0.020
H0086**	yes	66	0.005	0.470	0.083	0.016	0.690	0.434	...	...	...	...	...	0.028
H0117*	no	9	...	0.124	0.014	0.048	0.081	0.044	0.012	0.310	...	...	0.218	...
H0118*	no	48	...	...	...	0.098	0.520	0.376	0.122	...	...	...	...	...
H0120*	no	30	0.003	0.730	0.123	0.086	0.280	0.157	0.081	0.014	0.002	0.012	0.019	0.005
J0028**	yes	17	0.003	0.348	0.288	0.043	0.093	0.061	0.328	0.012	0.001	0.038	0.007	0.113
J0105*	yes	39	0.105	0.027	0.009	0.143	0.462	0.234	0.114	...	...	0.025	...	0.020
J0119*	yes	8	0.001	0.005	...	0.024	0.068	0.060	0.008	...	...	0.022	...	...
J0132*	yes	11	0.007	0.004	...	0.013	0.121	0.062	0.008	...	...	0.079	...	...
K0027*	yes	65	0.003	0.948	0.705	0.154	0.505	0.378	0.035	0.008	...	...	...	0.124
K0049	yes	53	0.321	0.652	0.108	...	...	0.062	0.177	0.013	...	0.732	...	0.002
K0060**	no	33	...	0.868	0.129	0.001	0.235	0.141	0.006	0.009	...	...	...	0.004
K0061	yes	65	0.360	0.566	0.095	...	...	0.111	0.194	0.018	...	1.21	...	0.362
K0073	yes	65	0.378	0.718	0.131	0.002	0.003	0.104	0.225	...	...	...	...	0.078
K0083**	yes	81	0.006	0.354	0.071	0.010	0.796	0.515	...	...	...	0.994	...	0.059

K0087**	yes	23	...	0.002	0.001	0.068	0.248	0.176	0.106	...	...	0.394	...	...
K0107*	yes	74	0.008	0.248	0.032	0.007	0.655	0.481	0.025	...	...	0.140	...	0.005
K0125*	yes	15	0.001	0.009	0.004	0.060	0.180	0.090	0.052	...	...	0.092	0.002	...
K0136*	yes	14	...	0.001	0.001	0.045	0.166	0.077	0.032	...	...	0.130	...	0.013
L0053**	yes	64	...	0.445	0.090	0.014	0.560	0.498	...	...	...	...	...	0.028
L0055*	yes	56	...	0.298	0.058	0.010	0.560	0.623	0.010	0.008	...	...	0.004	0.012
L0063**	yes	58	...	0.382	0.059	0.007	0.576	0.503	...	...	...	...	...	0.035
L0081**	yes	75	...	0.413	0.085	0.013	0.809	0.672	0.010	...	...	...	...	0.040
L0091*	yes	72	...	0.047	0.002	0.271	0.912	0.501	0.362	...	...	0.027	0.012	0.053
L0093*	yes	75	...	...	0.004	0.305	0.901	0.556	0.392	...	...	...	0.011	0.006
L0099*	yes	76	...	0.015	...	0.201	0.882	0.620	0.369	...	...	...	...	0.005
L0100*	yes	78	...	0.009	0.002	0.271	0.948	0.690	0.253	...	...	0.004	...	0.012
L0101*	yes	76	0.004	0.077	0.017	0.286	0.911	1.14	0.236	0.021	...	0.002	0.015	0.069
L0124*	yes	84	...	0.033	0.009	0.267	0.844	0.650	0.157	0.010	...	0.010	...	...
L0131*	yes	81	0.002	0.002	...	0.150	0.836	0.592	0.186	...	...	...	...	0.005
L0135*	yes	78	0.008	0.023	0.015	0.319	0.958	0.673	0.249	...	...	...	...	0.023
L0140**	yes	81	0.001	0.593	0.081	0.085	0.572	0.113	...	...	...	0.034	...	0.051
						Titanium-Based Paints								
A0002**	no	98	0.004	0.244	0.003	0.012	0.030	0.016	0.002	...	...	...	...	0.042
A0033**	no	152	0.002	0.277	0.009	0.050	0.097	0.045	0.007	...	...	...	...	0.037
A0042	no	78	0.016	0.171	...	...	0.013	...	0.008	...	...	...	...	0.004
A0044	no	140	0.051	0.163	...	...	0.048	...	0.029	...	...	...	...	0.020
A0121**	no	125	...	0.159	0.009	0.058	0.107	0.064	0.019	0.002	...	...	...	0.004
A0122*	no	170	0.002	0.168	0.005	0.040	0.061	0.050	0.026	0.007	...	...	0.003	0.011
A0123*	no	126	0.004	0.158	0.016	0.065	0.097	0.057	0.046	...	...	0.001	0.002	0.004
B0057	yes	604	0.262	0.179	...	...	...	...	0.862	...	0.185	...	0.009	0.077
B0072	yes	679	0.456	0.159	...	...	0.793	...	0.223	0.005	...	...	...	0.089
H0005*	no	251	0.005	0.329	0.041	0.130	0.551	0.080	0.031	0.004	...	...	0.003	0.050
H0006**	no	188	0.026	0.418	0.094	0.047	0.044	0.012	0.424	0.004	...	...	...	0.182
H0008*	no	233	0.006	0.263	0.088	0.045	0.088	0.026	...	1.14	0.006	...	0.882	0.058
H0035**	no	202	...	0.297	0.013	0.092	0.215	0.006	0.002	...	...	...	0.002	0.047
H0037**	no	142	0.026	0.246	...	...	...	...	0.108	...	...	...	...	0.097
H0065**	no	185	0.004	0.158	0.001	0.110	0.328	0.079	...	...	...	...	...	...
H0079**	no	121	0.019	0.120	...	...	0.036	...	...	...	...	...	...	...
H0108*	no	387	0.002	0.181	0.189	0.264	0.953	0.167	0.129	1.13	...	0.058	0.882	0.009
K0058**	no	378	...	0.145	...	0.271	0.832	0.174	...	...	...	0.017	0.003	0.016
K0064	yes	104	0.592	0.168	...	...	0.877	0.005	0.229	...	...	0.433	...	0.572
K0104*	no	149	0.002	0.159	0.027	0.073	0.089	0.062	0.030	0.177	...	...	0.134	...

TABLE 1—*Continued.*

Sample	Metallic Paint	Counting Time, s	Ca	$Ti-K_\alpha$/ $Ba-L_\alpha$ Ratio	$Ti-K_\beta$/ $Ba-L_\beta$ Ratio	Cr	Mn	Cu	Zn	$As-L_\alpha$/ $Pb-L_\alpha$ Ratio	$Se-K_\alpha$	$As-L_\beta$/ $Br-K_\alpha$ Ratio	$Pb-L_\beta$/ $Se-K_\beta$ Ratio	Sr
L0007	no	323	0.198	0.164	...	...	0.280	0.018	0.097	...	...	...	0.002	0.043
L0021**	no	183	0.004	0.407	0.028	0.057	0.076	0.044	0.005	...	...	...	...	0.098
L0045	yes	91	0.505	0.168	...	0.001	0.853	0.272	0.291	...	...	...	...	0.269
L0050	yes	917	0.725	0.170	...	...	0.893	0.059	0.336	...	...	...	...	0.626
L0069	no	550	0.439	0.168	...	...	0.580	0.036	0.178	...	...	...	...	0.060
L0098*	no	208	0.003	0.157	0.018	0.134	0.174	0.122	0.031	0.001	...	...	...	0.003
L0102*	no	518	0.002	0.150	0.111	0.547	0.617	0.460	0.252	...	...	...	...	...
L0103**	no	165	0.001	0.329	0.018	0.066	0.099	0.056	0.011	0.003	...	...	...	0.045
						Barium-Based Paints[b]								
B0018**	yes	55	0.003	0.744	0.104	0.256	0.385	0.167	0.037	0.005	...	...	...	0.192
B0020*	yes	62	0.003	0.721	0.122	0.255	0.355	0.129	0.013	...	...	...	0.010	0.202
C0001**	no	72	0.005	0.842	0.192	0.366	0.755	0.206	0.800	...	...	...	...	0.235
C0034**	no	47	0.005	0.852	0.126	0.176	0.181	0.216	0.843	...	...	0.070	0.005	0.356
E0017**	yes	41	...	0.501	0.129	0.104	0.171	0.107	0.007	...	...	...	...	0.301
F0030**	yes	55	0.002	0.868	0.128	0.185	0.529	0.102	1.03	0.003	...	...	0.022	0.404
H0029**	no	38	0.004	0.465	0.054	0.183	0.379	0.124	0.025	...	...	0.010	0.024	0.081
K0014*	yes	87	0.004	0.785	0.166	0.472	0.863	0.283	0.018	...	...	...	0.068	0.226
K0015**	yes	60	...	0.052	0.133	0.240	0.786	0.255	1.02	0.019	...	0.988	...	0.234
K0016**	yes	49	0.006	0.938	0.192	0.150	0.237	0.219	0.855	...	...	0.071	0.005	0.361
K0026**	yes	55	...	0.869	0.127	0.264	0.482	0.133	0.731	0.015	...	0.096	0.027	0.268
K0106*	yes	54	0.006	0.750	0.117	0.223	0.804	0.234	0.062	0.002	...	...	...	0.193
L0004**	yes	51	0.007	0.749	0.103	0.204	0.262	0.144	0.091	0.004	...	...	0.016	0.212
L0010**	yes	63	...	0.711	0.112	0.264	0.321	0.252	0.031	...	...	...	...	0.224
L0011*	yes	114	...	0.677	0.186	0.792	0.920	0.609	0.047	...	...	...	...	0.118
L0022*	yes	75	...	0.722	0.161	0.418	0.485	0.323	0.018	...	...	...	...	0.138
L0023*	yes	64	...	0.723	0.134	0.332	0.408	0.387	0.023	0.020	...	...	...	0.175
						Lead-Based Paints								
E0003**	no	51	...	0.010	0.016	0.100	0.020	0.028	0.005	0.063	1.26	0.014	0.005	0.028
E0024**	no	93	0.002	0.141	0.127	0.129	0.041	0.030	0.016	0.002	1.28	0.011	0.001	0.072
E0046	no	103	0.011	0.039	0.014	0.118	0.018	0.044	...	0.013	1.33	0.012	0.002	0.044

E0054	no	200	0.052	0.071	0.019	0.137	0.019	0.091	...	0.046	1.36	0.009	...	0.024
E0076	no	132	0.020	0.031	0.012	0.123	0.021	0.040	...	0.030	1.33	0.010	0.001	0.023
E0094*	no	141	0.001	0.014	0.008	0.140	0.104	0.099	0.062	0.027	1.34	0.007	...	0.019
E0095**	no	234	...	0.008	0.003	0.193	0.219	0.206	0.106	0.075	1.30	0.006	0.005	0.023
E0096**	no	108	0.002	0.075	0.071	0.138	0.046	0.027	0.019	0.007	1.32	0.014	0.005	0.041
G0019	no	180	0.037	0.175	0.023	0.112	...	0.409	...	0.009	1.33	0.010	...	0.083
G0056	yes	393	0.208	0.508	0.096	0.137	0.020	0.355	...	0.130	1.34	...	...	0.232
G0070	no	62	0.002	0.016	0.003	0.113	0.018	0.018	...	0.004	1.30	0.012	0.002	0.008
G0115*	no	138	0.002	0.095	0.076	0.150	0.064	0.909	0.028	0.008	1.31	0.010	0.005	0.036
H0043	no	254	0.064	0.950	0.156	0.106	0.004	0.136	...	0.034	1.32	0.006	...	0.025
H0067	no	204	0.045	0.967	0.154	0.079	0.009	0.040	...	0.033	1.27	0.010	...	0.022

[a] EDX conditions: 4000 counts Fe (K_α); 34.0 kV; 3.00 mA; rhodium filter; indium collimator; air path; and dead time, approximatley 35 to 40%. Samples: single asterisk (*) indicates aluminum panels with electrolytically deposited copper; double asterisk (**) indicates aluminum panel. If K_β/K_α of Ti > 0.165, then Ba is present; if K_β/K_α of Ti < 0.730, then Ti is present.

[b] As-L_α/Pb-L_α, As-L_β/Br-K_α, and Pb-L_β/Se-L_β are emission energies which overlap with a complexity that does not allow precise extrapolation in the barium-based paints.

TABLE 2—*Elemental distribution in the NBS 1974* Automotive Colors.

	Ca	Ti	Ba	Cr	Mn	Fe	Cu	Zn	As	Se	Br	Pb	Sr
Samples, no.	86	100	60	117	120	138	115	121	19	18	31	32	121
Samples, %	61.4	71.4	42.8	83.6	85.7	98.6	82.1	86.4	13.6	12.8	22.1	22.8	86.4
Titanium-based paints, %	60.7	100	35.7	57.1	64.3	92.8	78.6	85.7	3.6	7.1	14.3	17.8	85.7
Barium-based paints, %	58.8	41.2	100	100	100	100	100	100	14.3	0	35.7	0	100
Iron-based paints, %	48.8	68.8	31.2	87.5	90	100	87.5	82.5	11.2	3.8	35	13.8	82.0
Lead-based paints, %	85.7	85.7	57.1	100	92.8	100	42.8	100	57.1	92.8	57.1	100	100

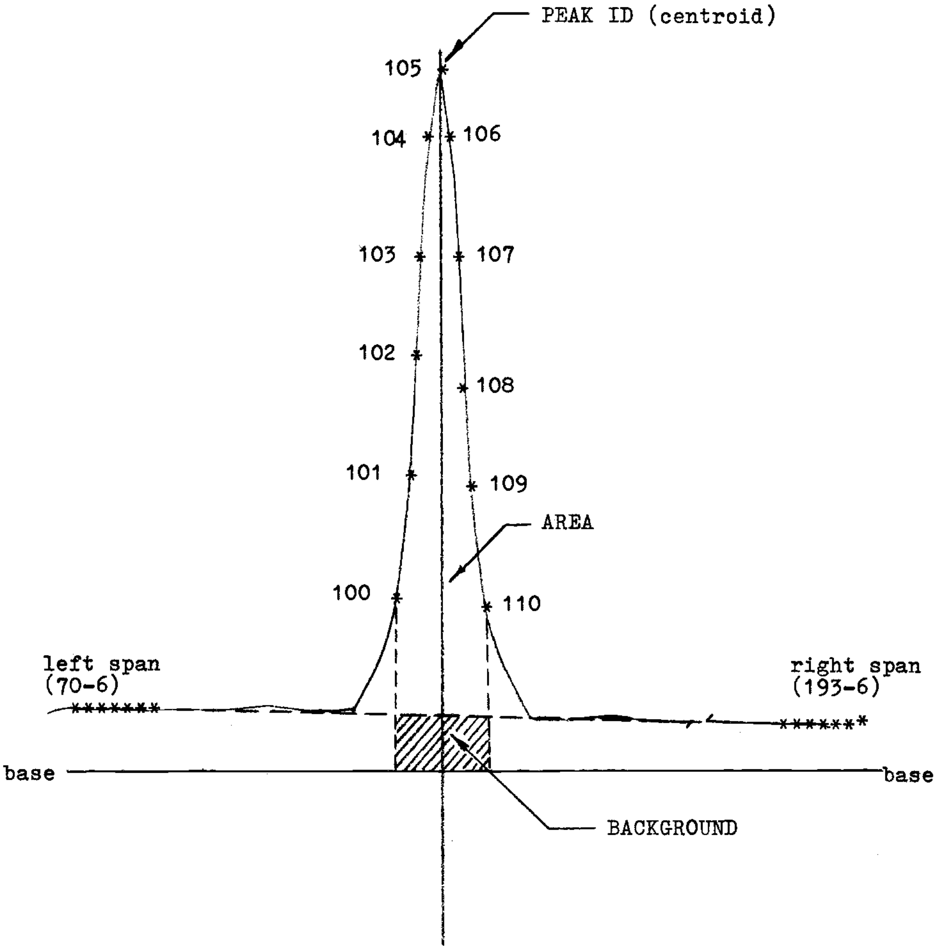

FIG. 1—*Diagram of the determination by computer of area and background counts for titanium* K_α *peak at 100-11.*

background as possible. The criteria were readily met in the calcium through copper region of the spectrum. The bremsstrahlung region, however, required division of the background into four regions favoring the elements in each division. The specifications for the peak spans are listed in Table 3.

It is important to note that peak area count is not based solely on the peak span of the specified elemental peak. The varying altitudes of the right and left spans, especially in the bremsstrahlung region, are troublesome. In the preliminary assignments of the peak spans, an attempt was made to establish the optimum right and left spans to minimize the extreme variation of peaks with a high signal to noise ratio. All the preceding operating conditions were entered into the minicomputer's memory core, and the analyses of the paint samples were initiated by the developed program.

Results

All paint samples were analyzed in reference to their predominant element. The program for each category used the same net ratios and was devised to limit the analysis of each sample to a preset number of counts for the respective base elemental peak. The

TABLE 3—*Elemental peak spans incorporated into the general paint analysis program (all peaks listed are K_α unless otherwise stated).*

Peak	Right Span	Left Span
1, Ca 75-11	193-6	70-6
2. Ti 100-11 Ba-L_α	193-6	70-6
3. Ba-L_β 113-11	193-6	70-6
4. Cr 126-11 Ba-L_γ 130-4	193-6	70-6
5. Mn 140-11	193-6	70-6
6. Fe 155-11	193-6	70-6
7. Cu 203-11	290-3	168-6
8. Zn 220-11	290-3	168-6
9. As 275-11 Pb-L_α	290-3	193-6
10. Se 294-11	365-4	260-3
11. As-K_β 309-11 Br 314-11	365-4	260-3
12. Pb-L_β 335-11 Se-K_β 332-11	365-4	260-3
13. Sr 380-11	446-4	365-4

elemental peaks chosen to represent these elements were the iron K_α, titanium K_α, barium L_α, and lead L_β peaks. This approach allows specimens of different sample size to be compared directly. In a few cases, the base element was in such high concentration that the analysis was completed in less than 10 s; in other instances 600 to 1500 s were required to complete the analysis.

A 600-s analysis is statistically more acceptable than a 10-s analysis, but the latter is not without value even though it has a larger statistical range. The longer analysis times were unusual in the large paint population studied, which required an average analysis time of 114 s. The statistical importance for each count of an analysis is dependent on a large number of variables because of drift in instrumental components and operating conditions. Specifically, these include X-ray tube potential and current, intensity and distribution of X-ray emissions, detector's electronic noise, and ADC dead time instabilities [*7*].

The statistical range considered for any single count is $(N \pm 2\sqrt{N})/(N' \pm 2\sqrt{N'})$ where N is any elemental count considered and N' is the base elemental count. For replicate analyses the statistical range is $\bar{N}$ and $\bar{N}'$, with the 2σ value applied as above.[2] The point scatter for each element is considered to be within two standard deviations of the true value or the quality of statistical precision expresses a 95% confidence level [*2*,Sec. 3.3(a)].

The approach was inadequate for low count rates; therefore, after further experimentation, we found that a questioned elemental count could be verified by submitting a sample to replicate analysis. A minimum of three runs was conducted to average a low count, calculate a 2σ value, and observe whether any single count exceeded the range. If the counts exceeded the range intermittently, it was considered that the background varied to the point that the element's presence could not be confirmed.

System Stability

The stability of the system was examined before the comparative analyses were tabulated. Three samples were analyzed 2½ months after the original analyses. Repeatability of results using the ratio technique was excellent.

[2]Personal communication, James Mathieson, Finnigan Corp.

Homogeneity of Paint Samples

Paint samples being compared elementally must be homogeneous within a batch formulation for the analysis to have any significance. Taking selected samples, analyses were conducted with a molybdenum minicollimator to limit the analysis area on three positions approximately 20 mm apart on each paint chip. In all samples, the ratio ranges were within the defined 2σ values. Table 4 and Fig. 2 illustrate the homogeneity of Sample 74E0003.

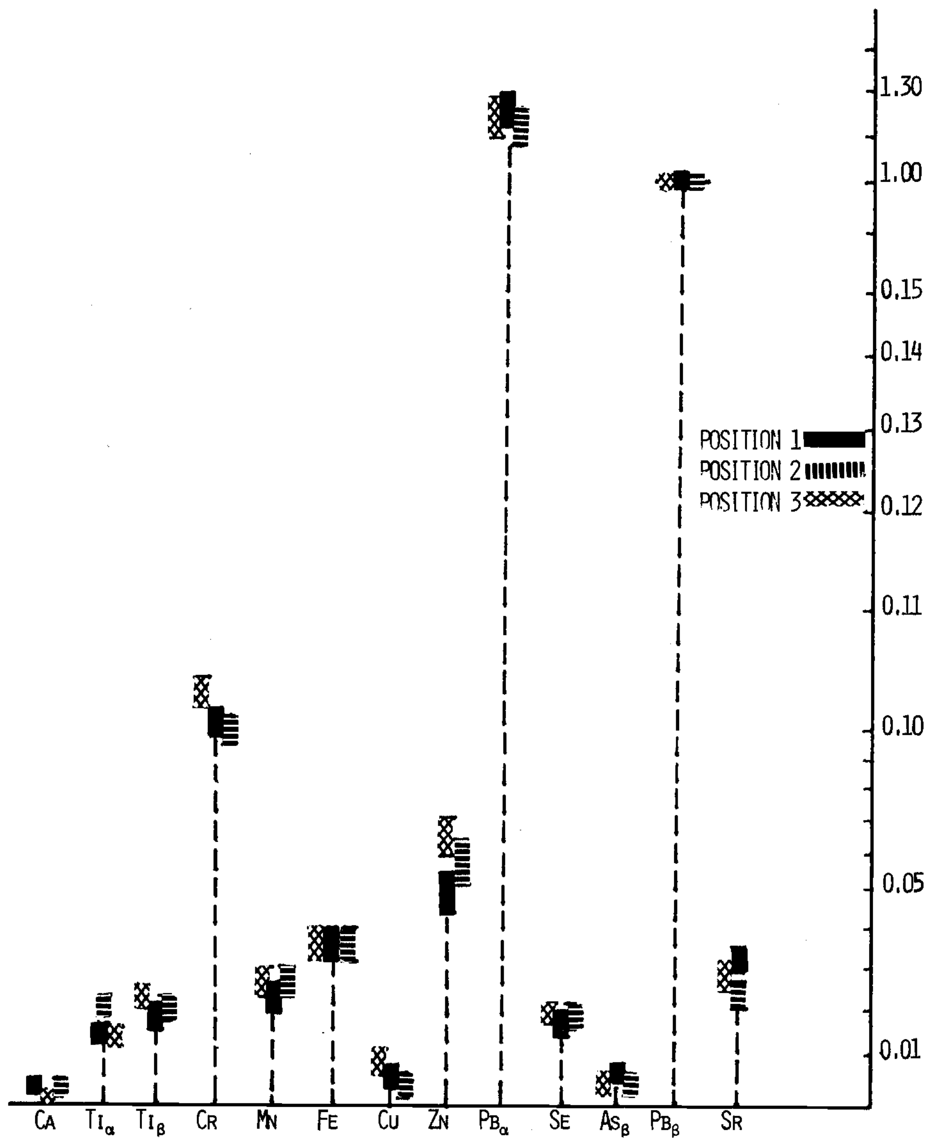

FIG. 2—*Graph showing the homogeneity of sample constituents for Positions 1, 2, and 3 for Sample 74E0003.*

TABLE 4—*Homogeneity of sample constituents as shown by range of ratios for Sample 74E0003.*

	Position 1		Position 2		Position 3	
Element	High	Low	High	Low	High	Low
Ca	0.002	0.001	0.002	0.001	0.000	0.000
Ti_α	0.014	0.012	0.017	0.015	0.016	0.013
Ti_β	0.020	0.016	0.020	0.017	0.022	0.019
Cr	0.103	0.096	0.102	0.094	0.110	0.101
Mn	0.022	0.019	0.025	0.021	0.024	0.020
Fe	0.035	0.030	0.035	0.030	0.034	0.030
Cu	0.007	0.005	0.005	0.004	0.008	0.006
Zn	0.050	0.042	0.056	0.050	0.058	0.057
Pb_α	1.28	1.22	1.25	1.20	1.27	1.22
Se	0.016	0.013	0.017	0.014	0.018	0.015
As_β	0.004	0.003	0.005	0.004	0.004	0.003
Pb_β	base	base	base	base	base	base
Sr	0.032	0.028	0.028	0.021	0.029	0.025

Homogeneity of Similarly Catalogued Paints from Different NBS Collections

Because two sets of the NBS *Automotive Colors* were available, the authors were able to analyze selected samples from different collections. Three samples (74E0068, 74E0003, 74A0044) from each set were analyzed and their net ratios were compared; in general, the ratios overlapped. In the cases where overlap did not occur, the 2σ values were within 5 to 10% of the lower ratio; although these small differences exist, the paint samples most probably have the same elemental profile.

Comparison of Similarly Colored Paints

The paint samples were compared visually for similar color and metallic flaking. Table 5 lists the samples that had similar colors. The samples were removed from their plastic folders for easy overlay, placed on a dull white background, and compared under indirect sunlight. They were also observed on the stage of a stereobinocular microscope at $\times 7$ to $\times 30$.

The categories that were chosen to be displayed in graphic form were generally the largest populations. The colors of the paints in each category were not exact matches, and slight variations in the texture of the metallic flaking were also observed, but samples were not excluded on that basis. Figures 3–8 and Tables 6–11 illustrate the elemental profiles of similarly colored paint samples from randomly selected categories. Visually similar samples in each color class are easily separated by their elemental composition with the exception of those samples in Fig. 8 and Table 11.

Comparison of the paints was usually based on a single analysis, as the repeatability of the system permitted the observation of gross elemental differences. Where only minor differences were observed, replicate analyses were made. If the samples were not discriminated it was necessary to go "off program" and to analyze the samples for their total elemental profile. It is important to note that the twelve element program is a method of elimination, as illustrated in Figs. 3–8 and Tables 6–11. Additional analyses should be conducted before paint samples of similar elemental composition are reported as being physically and chemically the same.

A common consideration in the analysis of paint by EDX is the introduction of interfering elements from undercoat layers and any supporting backing. The presence of aluminum backing on samples in this study caused elevated levels of chromium, manganese,

TABLE 5—*Paint standards from* Automotive Colors *that were indistinguishable by color.*

White, nonmetallic flaking, Group 1
- Ti A0044—see Table 6, Fig. 3
- Ti A0122
- Ti A0123

White, nonmetallic flaking, Group 2
- Ti A0033
- Ti A0121

Gray, metallic
- Ti B0057
- Fe B0052
- Fe B0092
- Fe B0129

Black, nonmetallic flaking, Group 1
- Ba C0001
- Ba C0034

Black, nonmetallic flaking, Group 2
- Fe C0041—see Table 7, Fig. 4
- Fe C0090

Red, nonmetallic flaking
- Pb E0003—see Table 8, Fig. 5
- Pb E0024
- Pb E0046
- Pb E0054
- Pb E0094

Red, metallic
- Fe E0068—see Table 9, Fig. 6
- Fe E0085
- Fe E0130

Brown, metallic, Group 1
- Fe F0012
- Fe F0040
- Fe F0127
- Fe F0133

Brown, metallic, Group 2
- Fe F0032
- Fe F0074
- Fe F0111
- Fe F0126

Brown, metallic, Group 3
- Fe F0013
- Fe F0110

Brown, metallic, Group 4
- Fe F0038
- Fe F0139

Brown, metallic, Group 5
- Fe F0128
- Fe F0134

Yellow, nonmetallic flaking, Group 1
- Ti H0008
- Ti H0037

Yellow, nonmetallic flaking, Group 2
- Ti H0035—see Table 10, Fig. 7
- Ti H0079

Green, metallic
- Ba K0106
- Fe K0061

Blue, metallic, Group 1
- Fe L0124
- Fe L0131

Blue, metallic, Group 2
- Fe L0100—see Table 11, Fig. 8
- Fe L0135

iron, and zinc. In fact, most of the samples tabulated in Table 2 contain these elements. The increases so introduced were observed to be on the order of 0.010 to 0.060 of the base elements, significant enough to alter the paint specimen's elemental profile but not enough to interfere with programmed analysis. Net ratios are low enough to allow stripping of the aluminum spectrum from the paint spectrum, thus eliminating interferences introduced by the backing. Interelement effects due to the aluminum backing are insignificant and do not interfere with comparative analysis of the paint samples.

Conclusion

It is evident to those observing the qualitative and semiquantitative compositions of the 1974 U.S. automotive paints that certain elements are common to many paints in a sufficiently wide variety of concentrations to discriminate among similarly colored samples.

Perhaps one of the most crucial aspects considered in the study was the homogeneity of the elemental components of the paint panels. Samples were found to be homogeneous within themselves and among panels prepared from the same paint source. In an approximation of real-case situations, paint specimens were subjected to analyses identical to routine paint analysis in a forensic laboratory.

In only two instances were the authors unable to discriminate by programmed analysis

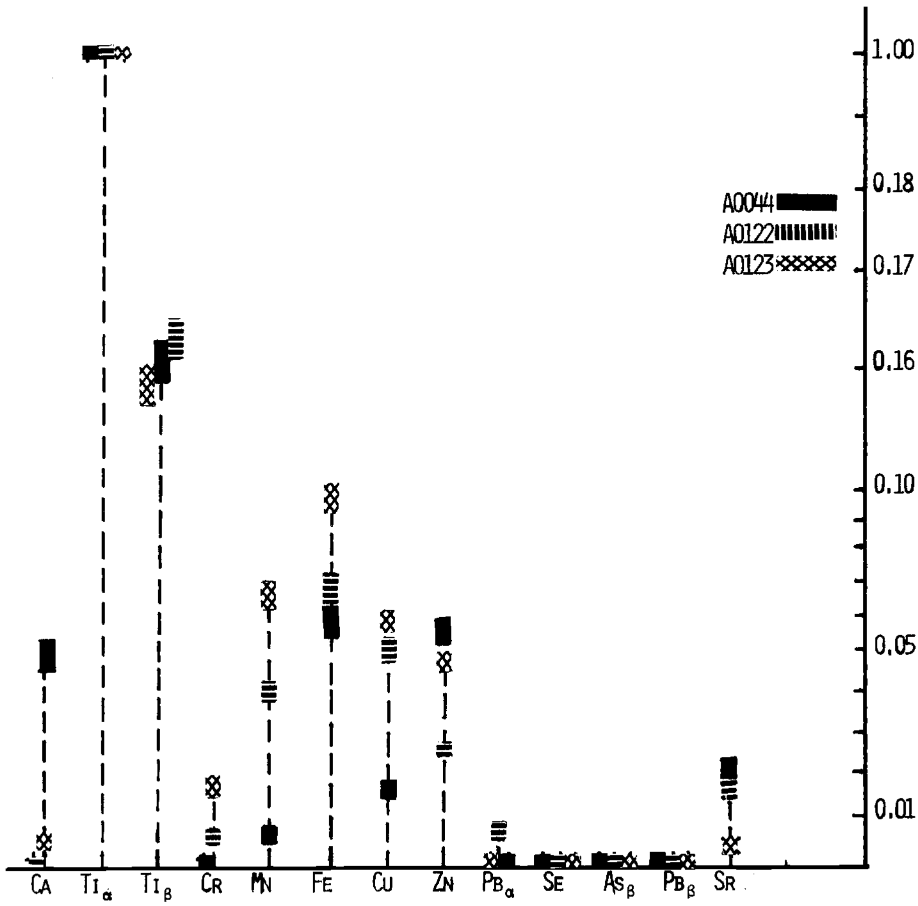

FIG. 3—*Graph of the range of ratios for three, white, titanium-based paint samples (see Table 6).*

TABLE 6—*Range of ratios for three, white, titanium-based paint samples (see Fig. 3).*

Element	Range of Ratios	
	High	Low
	A0044[a]	
Ca	0.054	0.048
Ti	base	base
Ti_β	0.169	0.158
Mn	0.006	0.003
Fe	0.050	0.045
Cu	0.019	0.014
Zn	0.031	0.027
Sr	0.016	0.011
	A0122	
Ti	base	base
Ti_β	0.174	0.162
Cr	0.006	0.004
Mn	0.043	0.038
Fe	0.064	0.058
Cu	0.053	0.047
Zn	0.028	0.024
Pb_α	0.008	0.006
Pb_β	0.003	0.002
Sr	0.012	0.010
	A0123	
Ca	0.005	0.003
Ti	base	base
Ti_β	0.164	0.152
Cr	0.017	0.014
Mn	0.068	0.062
Fe	0.101	0.093
Cu	0.060	0.054
Zn	0.049	0.044
Sr	0.004	0.003

[a]This sample had an aluminum-copper backing applied to it so that the three samples could be compared uniformly.

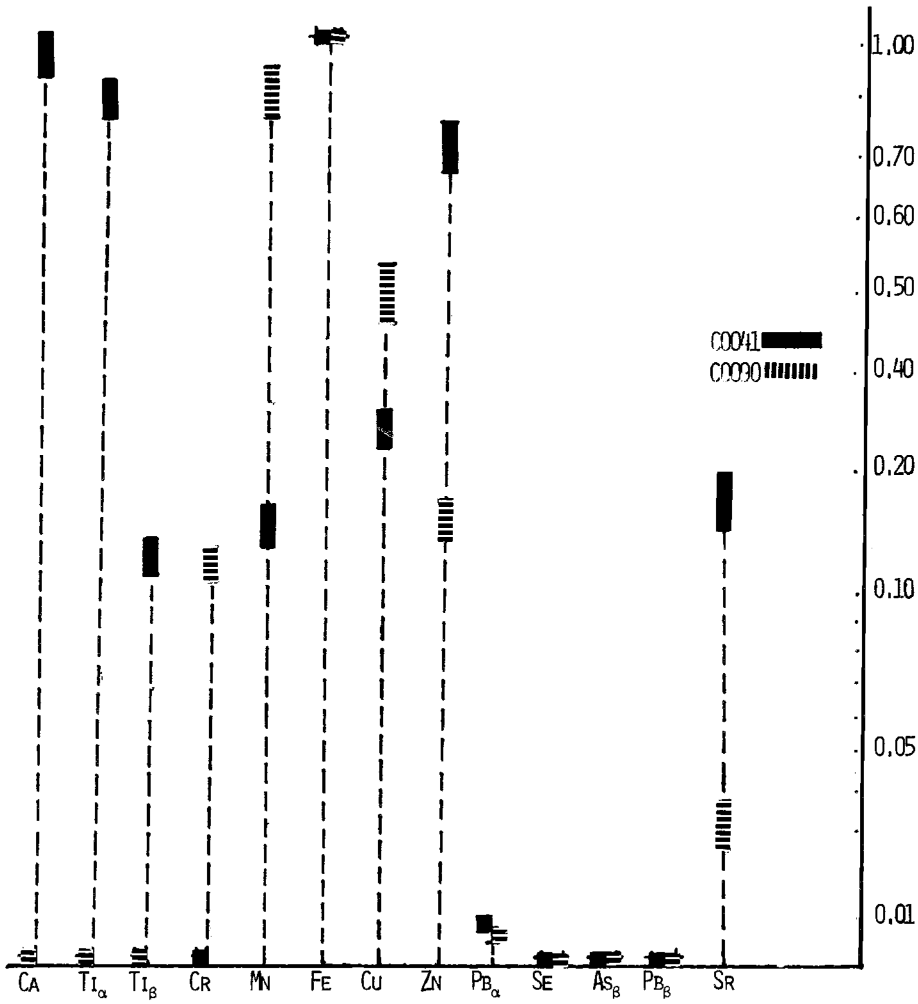

FIG. 4—*Graph of the range of ratios for two, black, iron-based paint samples (see Table 7).*

TABLE 7—*Range of ratios for two, black, iron-based paint samples (see Fig. 4).*

Element	Range of Ratios	
	High	Low
	C0041[a]	
Ca	0.832	0.786
Ti	0.723	0.688
Ti_β	0.165	0.129
Mn	0.197	0.145
Fe	base	base
Cu	0.294	0.262
Zn	0.720	0.652
As_α	0.007	0.003
Sr	0.200	0.154
	C0090	
Cr	0.153	0.121
Mn	0.780	0.680
Fe	base	base
Cu	0.534	0.458
Zn	0.193	0.160
As_α	0.009	0.004
Sr	0.035	0.022

[a]This sample had an aluminum-copper backing applied to enable uniform comparison.

between similarly colored paint samples from known sources. Paint samples E0024 and E0094 were similar when analyzed by the general program; when studied "off program," the two samples were shown to contain molybdenum. However, the respective net ratio differences established that the paint samples were not of a common origin (Fig. 5 and Table 8). Paint specimens L0100 and L0135 exhibited similar elemental compositions. Replicate "off program" and organic analyses indicated that the samples were from a common origin (Fig. 8 and Table 11). Manufacturer's information as outlined in Section 1 of *Automotive Colors* and information from NBS confirmed the samples' common origin.

Summary

Elemental, qualitative, and semiquantitative analyses of 1974 U.S. automotive paints by a Finnigan Model 900F Energy Dispersive X-ray (EDX) Spectrometer are examined. This EDX analytical system incorporates a minicomputer to receive, store, and present data. The paint samples were received from the National Bureau of Standards (NBS) Law Enforcement Standards Laboratory as a collection representative of the top coats used on all U.S. manufactured automobiles in 1974.

Aspects considered include EDX system stability, homogeneity of similarly catalogued samples from different NBS collections, categorization of paints by predominant constituents, and comparison of data on paint standards that were similar.

Automated analysis represents an important application of forensic science to the characterization of paint samples and provides for the nondestructive analysis of a variety of materials in a large range of sample sizes and concentrations.

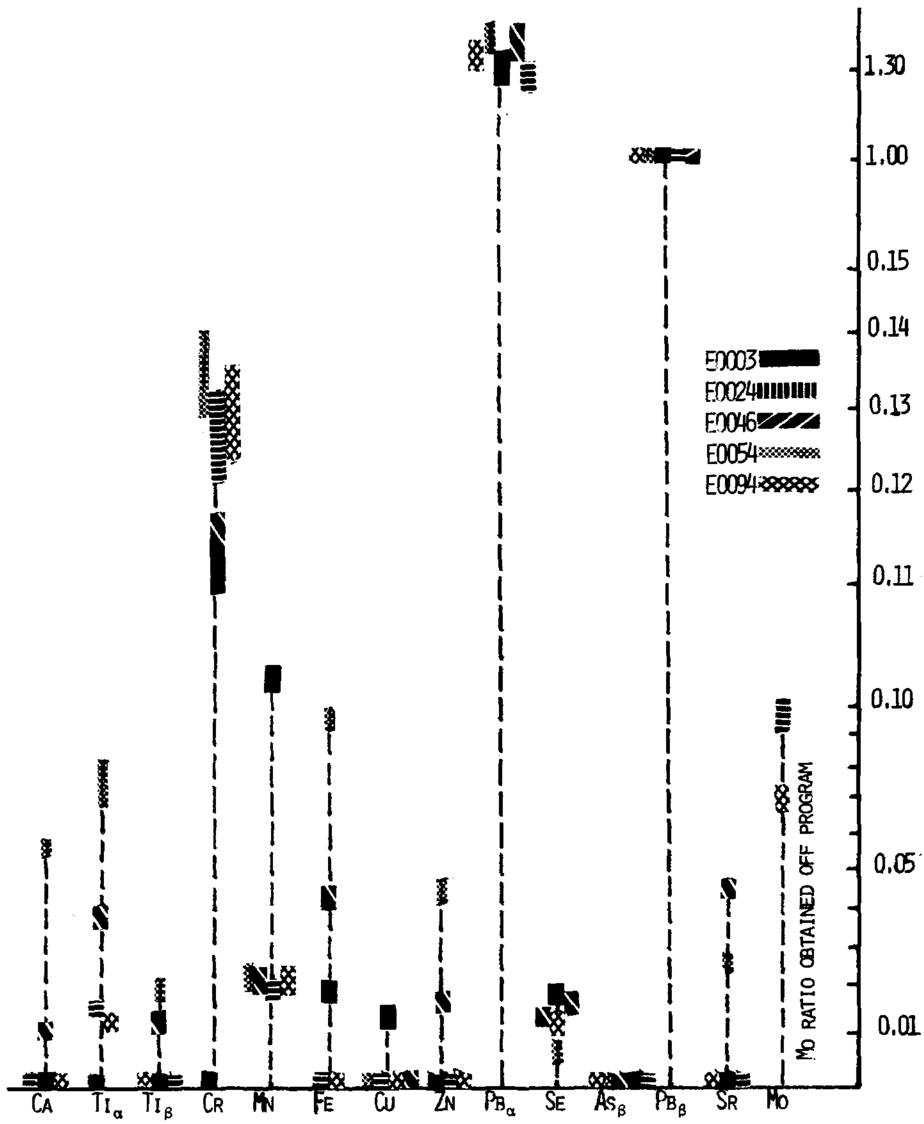

FIG. 5—*Graph of the range of ratios for five, red, lead-based paint samples (see Table 8).*

TABLE 8—*Ranges of ratios for five, red, lead-based paint samples (see Fig. 5).*[a]

Element	Range of Ratios	
	High	Low
	E0003	
Mn	0.110	0.102
Fe	0.019	0.014
Cu	0.023	0.018
Pb_{α}	1.36	1.26
Se	0.019	0.015
Pb_{β}	base	base
	E0024	
Ti_{α}	0.018	0.013
Cr	0.132	0.125
Mn	0.018	0.014
Pb_{α}	1.36	1.26
Se	0.019	0.014
Pb_{β}	base	base
Mo	0.099	0.092
	E0046	
Ca	0.013	0.010
Ti	0.042	0.037
Ti_{β}	0.016	0.013
Cr	0.123	0.113
Mn	0.019	0.016
Fe	0.047	0.042
Zn	0.015	0.012
Pb_{α}	1.36	1.31
Se	0.013	0.011
As_{β}	0.002	0.002
Pb_{β}	base	base
Sr	0.047	0.042
	E0054	
Ca	0.055	0.049
Ti	0.075	0.068
Ti_{β}	0.021	0.018
Cr	0.143	0.132
Mn	0.020	0.017
Fe[b]	0.095	0.087
Zn	0.049	0.043
Pb_{α}	1.39	1.34
Se	0.010	0.007
Pb_{β}	base	base
Sr	0.026	0.022
	E0094	
Ti_{α}	0.016	0.012
Cr	0.135	0.116
Mn	0.021	0.017
Pb_{α}	1.36	1.30
Se	0.018	0.014
Pb_{β}	base	base
Mo	0.071	0.065

[a] Samples were removed from their respective backings to enable uniform comparison.

[b] Copper and As_{β} were not present.

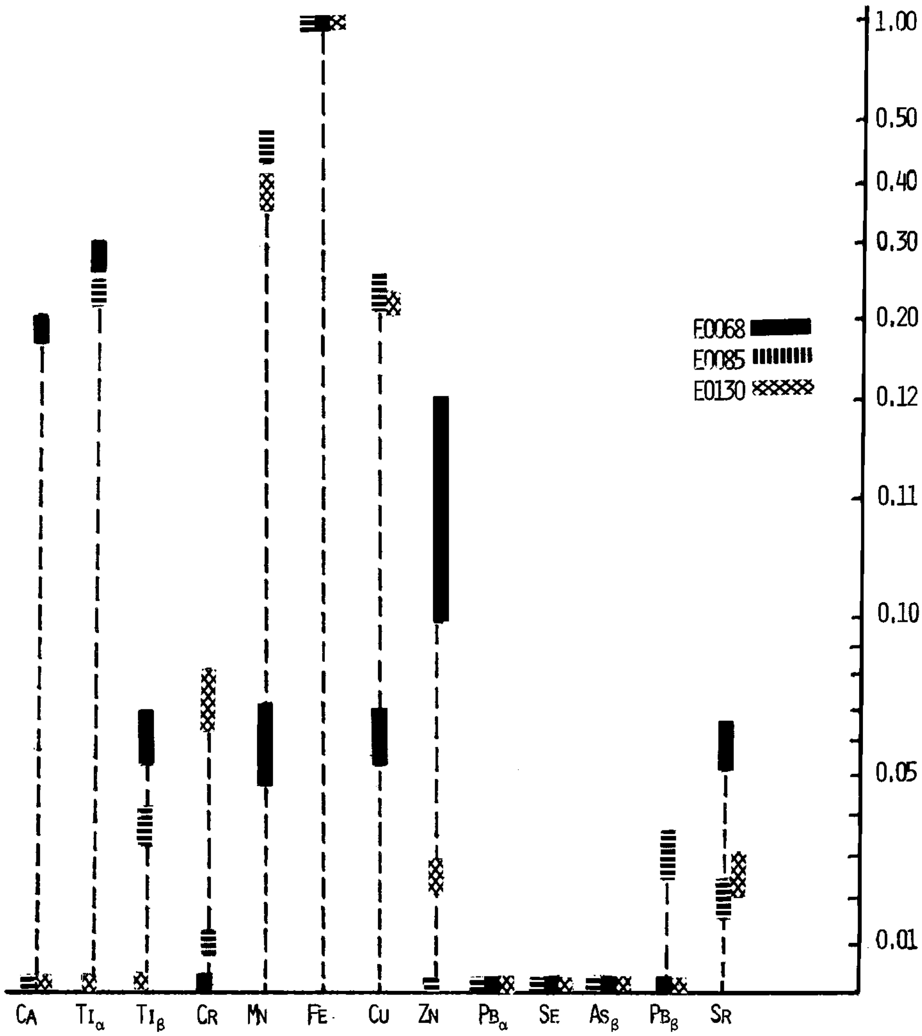

FIG. 6—*Graph of the range of ratios for three, red, iron-based paint samples (see Table 9).*

TABLE 9—*Range of ratios for three, red, iron-based paint samples (see Fig. 6).*

Element	Range of Ratios	
	High	Low
	E0068[a]	
Ca	0.220	0.178
Ti	0.349	0.293
Ti_β	0.068	0.049
Mn	0.075	0.045
Fe	base	base
Cu	0.070	0.050
Zn	0.126	0.098
Sr	0.066	0.050
	E0085	
Ti	0.272	0.225
Ti_β	0.045	0.030
Cr	0.014	0.007
Mn	0.507	0.434
Fe	base	base
Cu	0.247	0.203
Pb_β	0.038	0.025
Sr	0.027	0.017
	E0130	
Cr	0.081	0.059
Mn	0.420	0.356
Fe	base	base
Cu	0.241	0.197
Zn	0.029	0.018
Sr	0.035	0.023

[a]This sample had an aluminum-copper backing applied to enable uniform comparison.

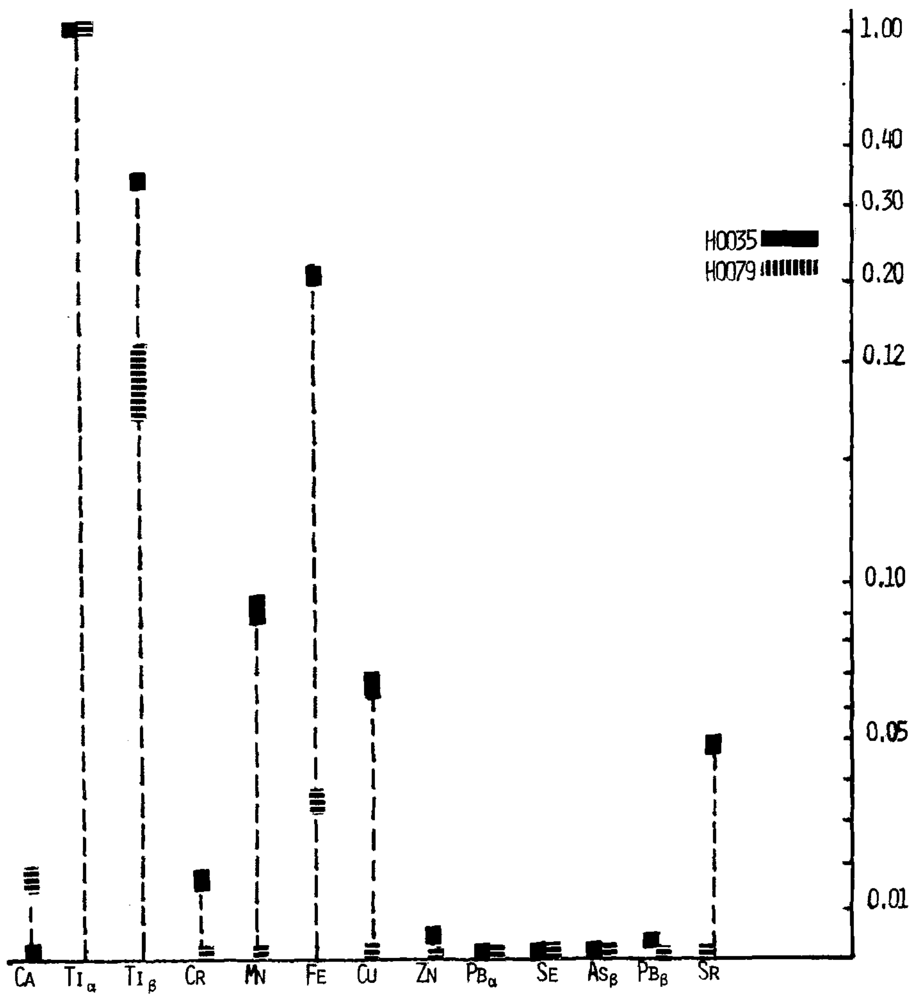

FIG. 7—*Graph of the range of ratios for two, yellow, titanium-based paint samples (see Table 10).*

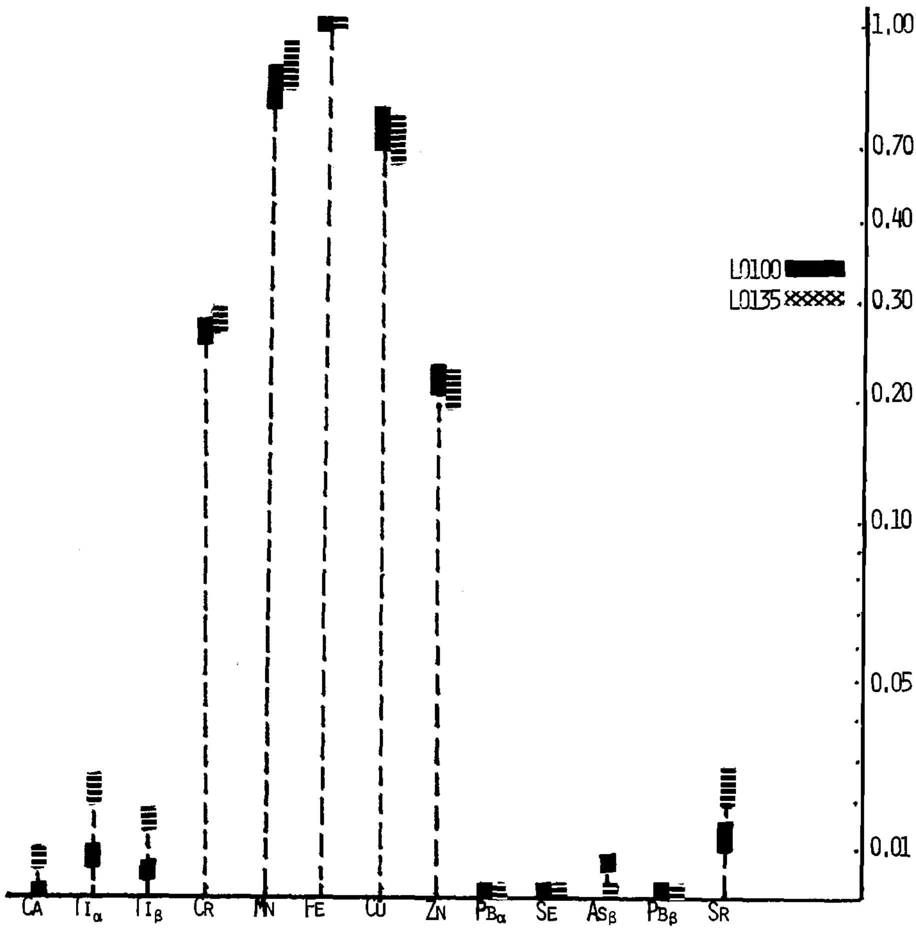

FIG. 8—*Graph of the range of ratios for two, blue, iron-based paint samples (see Table 11).*

TABLE 10—*Range of ratios for two, yellow, titanium-based paint samples (see Fig. 7).*

Element	Range of Ratios	
	High	Low
	H0035	
Ti	base	base
Ti_{β}	0.306	0.289
Cr	0.014	0.012
Mn	0.096	0.088
Fe	0.222	0.208
Cu	0.069	0.063
Zn	0.003	0.002
Pb_{β}	0.002	0.001
Sr	0.050	0.045
	H0079	
Ca	0.021	0.017
Ti	base	base
Ti_{β}	0.125	0.115
Fe	0.038	0.034

TABLE 11—*Range of ratios for two, blue, iron-based paint samples (see Fig. 8).*

Element	Range of Ratios	
	High	Low
	L0100	
Ti	0.013	0.006
Ti_{β}	0.004	0.001
Cr	0.297	0.246
Mn	1.01	0.889
Fe	base	base
Cu	0.745	0.643
Zn	0.278	0.230
As_{β}	0.006	0.002
Sr	0.016	0.008
	L0135	
Ca	0.011	0.005
Ti	0.029	0.018
Ti_{β}	0.020	0.011
Cr	0.348	0.292
Mn	1.02	0.898
Fe	base	base
Cu	0.722	0.627
Zn	0.274	0.226
Sr	0.029	0.018

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