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Forensic Characteristics of Colored Polyethylene Bags

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ABSTRACT: The inorganic elemental profiles of colored polyethylene bags were determined by X-ray fluorescence spectroscopy. Homogeneity in single bags and reproducibility of bags in a batch were ascertained. The probability of an incorrect matching of two very similar yellow bag batches was found to be 10^{-9} to 10^{-8} , while a bag is attributed to its batch with a relatively high probability of the order of 1. These characteristics can be applied in the forensic examination of the colored polyethylene bags often used in drug abuse. Similar properties are reported for transparent polyethylene (no pigment additives), where the concentration of zinc was 0.6 ± 0.1 ppm.

KEYWORDS: criminalistics, polyethylene bags, forensic science

Colored polyethylene bags, which are offered to customers in grocery shops and at fruit and vegetable stands in markets, are often used in criminal activities associated with drug abuse.² Retail quantities of drugs are wrapped by drug dealers in pieces of colored polyethylene that have been cut from bags. The pieces are shaped into small envelopes that are sealed by means of a domestic heat source, for example, an iron, candle, cigarette lighter, etc.

Whenever these envelopes are seized, a search is made of the property of a suspected dealer. If a few colored bags are discovered in the search, the question is whether these are correlated with the seized drug envelope. The answer is straightforward negative if the colors do not match. However, if the colors are similar to the degree that by visual examination it is impossible to discriminate between the envelope and bags, then a reliable characterization method is required.

Colored polyethylene bags are manufactured by blending pigments in polyethylene. Blending of small quantities of pigments in large quantities of polyethylene is done by mechanical stirring. The blend is melted at 200°C and extruded to the required shape. Therefore, it is presumed that the bags are relatively homogeneous. This characteristic refers to a single batch of bags that is produced under fixed conditions. Due to deficiencies in the extruder, it is possible that the bags will have regions of a lighter color, resulting from reduced thickness of the bag material. These regions of lighter color

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²Personal communication, Israel Police, Division of Identification and Forensic Science, 1993.

extend along the bag, parallel to the direction of extrusion. However, the elemental composition in these regions is identical to that in other parts of the bag.

There is great variability in the production process among manufacturers, because of the different pigments and quantities used. Even within a particular production plant, variation occurs between lots of bags of similar color, because of the varying quantities of pigments and polyethylene blended under the different prevailing production conditions. This can be exemplified by the blending procedure, which involves a handful of pigment being introduced into a 25 kg sack of polyethylene.

On the other hand, the variability in a specific production lot is assumed to be very low because the production conditions are kept reasonably constant within the lot. This feature, which will be examined in this paper, is very important in criminal interrogation, because it is assumed that the drug dealer collects a few consecutive bags from a batch in a shop. His next step is to prepare the retailing envelopes from one or more bags of the batch. If the batch of bags is reproducible with respect to elemental composition, then profiling can be established and the bags and drug envelope can be discriminated.

The quantities used by bag manufacturers are of the order of 10 g of pigment per 25 kg of polyethylene.³ The weight concentrations of certain chemical elements in the bags are of the order of hundreds of ppm (parts per million). The detection, identification and measurement of inorganic components of pigments at this estimated concentration level can be conducted by various analytical methods.

Low-density polyethylene bags were compared by infrared spectroscopy [1]. Samples were matched on the basis of frequency, shape and relative intensity of weak infrared absorption bands. Colored and opaque bags were not examined owing to their strong pigment absorption superimposed on the polyethylene spectrum. Another drawback of this method was the requirement to have samples between 0.5 and 0.75 mm thick to intensify weak bands in the infrared spectra. Preparation of samples was a rather complicated procedure that involved film compression and heating under standard conditions.

Plastic garbage bags and sandwich bags were examined physically by observing the cut ends [2]. These characteristic marks could be related to sequentially made bags. In a similar approach, cut ends, holes, perforations and marks caused by home heat sealers, were investigated [3].

In the present work, the XRF (X-ray fluorescence) method was used for the characterization of colored polyethylene bags. This analytical method is based on the interaction between a primary exciting radiation (X-rays, electrons, protons, alpha particles) and the electrons in the atoms of the analyzed sample. The primary radiation can eject electrons from the innermost K or L orbitals and electrons from outer L, M orbitals can fill the vacancies. This process is accompanied by the emission of secondary fluorescent X-rays, the energy of which is equal to the difference between electron binding energies of the outer and inner orbitals. Therefore, the fluoresced X-rays by a specific chemical element have energies characteristic to this element.

XRF spectroscopy is a technique that enables the investigator to detect and identify quantitatively elements in the sample in question. Furthermore, a quantitative assay of the elemental composition can be performed, knowing the functional relation between the line intensity of an analyte element in the spectrum and the concentration of this element.

The dynamic range of the XRF method is very broad and concentrations from 100% down to sub-ppm levels are feasible, depending on the chemical element measured and the matrix in which it is embedded. Another advantage to this method is the simultaneous

³Personal communication, manufacturers of colored polyethylene bags, Rishon-Le-Zion, Israel, 1993.

analysis of most elements, from light metals (for example, aluminum) to the transuranics. No preliminary treatment is required and sample shape is irrelevant: bulk solid samples, liquids, tablets prepared from pressed powders, and dust collected on filter paper, can be measured easily. The XRF analysis is nondestructive and there are no residual effects induced in the sample; it is therefore impossible to detect that the sample has been tested.

Experimental

The System

A schematic drawing of the experimental system is presented in Fig. 1. The X-ray tube is a water-cooled high-power tube with a Mo anode and an optical point focus of $0.4 \text{ mm} \times 0.8 \text{ mm}$, offering good geometry in the exposure of small samples. The tube was operated at a high voltage of 27 kV and a current of 30 mA, furnished by the 60 kV, 4.8 kW X-ray generator. Its 0.1% high voltage and tube current stability offers good precision. A quartz filter between the X-ray tube and the sample, effectively eliminates the bremsstrahlung X-ray continuum emitted by the Mo anode. Therefore, the signal-to-background ratio was improved due to the nearly monoenergetic primary beam.

The 3 mm thick Si(Li) detector has an active area of 30 mm^2 . A $12.7\text{-}\mu\text{m}$ -thick beryllium window on the cryostat enables the measurement of light elements, for example, aluminum, where the X-ray energies are of the order of 1.5 keV.

Collimators were used in the beams' paths with the aim of defining the cross section of the primary beam that exposes the sample and tailoring the secondary beam to decrease incomplete charge collection effects at the detector edges, which can have a detrimental influence on peak resolution.

The energy resolution was 165 eV for the 5.9 keV Mn K_{α} line at a shaping time of $12 \mu\text{s}$ of the electronic amplifier. Electronic pulses were analyzed and spectra processed by a Tracor Northern TN-5400 multichannel analyzer.

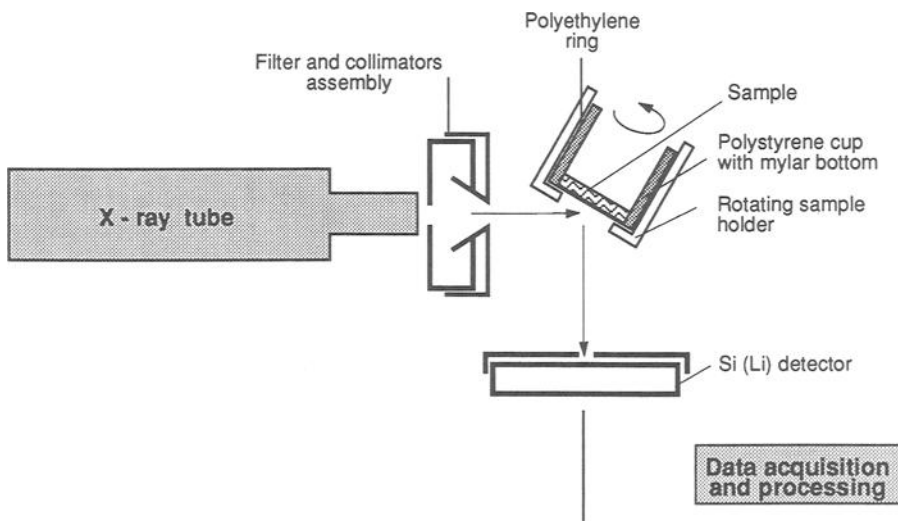


FIG. 1—*Experimental system.*

Samples

Colored polyethylene bags were collected at different locations, such as grocery and butcher shops, fruit and vegetable stands in a market, bakery, etc. These bags have two carrying loops and, because of their shape, are nicknamed 'A-Shirts.'

The thickness of a single layer of material was measured in several bags and found to average 0.016 mm; the density was 0.92 g/cm³.

Sampling the bags was effected by punching out discs, 10 mm in diameter, which were then placed in a measuring cup (see Fig. 1). In order to enhance the XRF signal, each sample consisted of 16 discs which were punched out from the double walled bag folded three times.

Various colored polyethylene bags were available: green, yellow, blue, pink, black, etc. Transparent polyethylene bags and sleeves (no pigments) were measured as well. Reproducibility and homogeneity of the element composition in the colored bags were determined by measuring successive bags in a batch and by sampling a specific bag at different regions.

Element concentrations in bags were measured by the 'standard addition' method. A standard stock solution of a specific element was prepared and small aliquots, of the order of 25 μ L, were pipetted onto the 10-mm-diam discs punched out from a bag. These samples were dried at room temperature and then counted. The functional relation of the number of counts in a XRF peak in the spectrum vs elemental mass was derived. This relation is usually linear, that is, the calibration curve is a straight line. The required concentration of an element in the bag is found from the zero-addition point on the curve.

Results and Discussion

The XRF spectrum of a yellow bag, acquired in 200 seconds, is shown in Fig. 2. The main peaks were assigned to: titanium, K α 4.51 keV; zinc, K α 8.64 keV; lead, L α 10.55 keV and L β 12.61 keV. Minor peaks were: calcium, K α 3.69 keV; chromium, K α 5.41

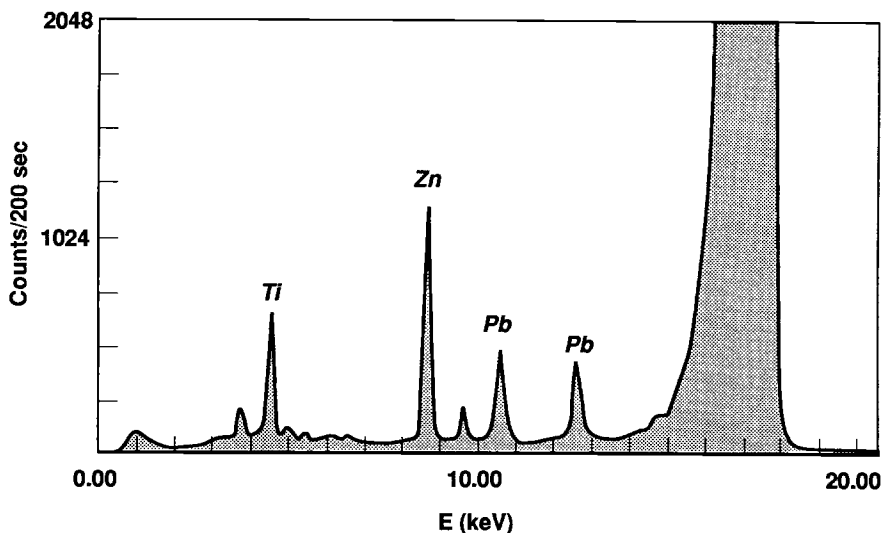


FIG. 2—XRF spectrum of a yellow bag typical for the first batch of bags.

TABLE 1—*Net peak areas (\pm S.D.) of chromium and lead in three samples of a yellow bag.*

Sample #	Cr, K_{α}	Pb, L_{α}
1	7973 \pm 100	101,444 \pm 333
2	7912 \pm 103	101,609 \pm 333
3	8085 \pm 102	101,493 \pm 335
Mean	7990 \pm 59	101,515 \pm 193

keV; iron, K_{α} 6.40 keV. Identification of peaks was based on their tabulated energies and the measured ratio between K_{α} and K_{β} , and L_{α} and L_{β} lines of an element.

The peaks were well resolved in the spectrum and could be used to determine quantitatively the element concentrations. Other, less abundant XRF lines could be identified as well, but these were not used in evaluating concentrations, because of their large statistical errors.

The homogeneity of pigment distribution in bags was determined by sampling a bag at three different locations. A yellow bag (different from the bag depicted in Fig. 2) gave the results shown in Table 1. Chromium and lead were evaluated because these were the main peaks in the measured spectrum, where the yellow color is based on the lead chromate pigment. The errors for the three samples quoted in Table 1 are standard deviations calculated using the gross and background numbers of counts under the relevant peaks. The Poisson distribution was used in this calculation. Uncertainties associated with the mean values in Table 1 were estimated from the standard deviations of the samples.

The variation in homogeneity of the pigment distribution in the bag was very small, of the order of 0.19%, when measured with three samples and monitored with the L_{α} peak of lead (Table 1). Similar results were obtained for other components of the spectrum. Hence, the bags are homogeneous with respect to chemical concentration and samples can be investigated independently of the location on the bag from which they were taken.

Reproducibility of element composition within a batch of bags was determined by measuring six yellow bags from one batch. These bags were drawn from the batch in two groups of three bags each, with an interval of five bags between the two groups. The spectrum shown in Fig. 2 pertains to a yellow bag of this batch. Net peak areas of several XRF lines, along with their standard deviations, were calculated for the six spectra. The results were almost uniform, within the experimental errors (Table 2), proving that the element composition is reproducible within this batch of bags.

Six bags of another yellow batch were sampled and measured similarly. The color

TABLE 2—*Net XRF peak areas (\pm S.D.) in six bags—batch #1.*

XRF Line	Y-1	Y-2	Y-3	Y-4	Y-5	Y-6
Ti, K_{α}	5472 \pm 90	5487 \pm 92	5644 \pm 90	5319 \pm 89	5392 \pm 88	5136 \pm 88
Zn, K_{α}	11,723 \pm 120	11,754 \pm 121	11,335 \pm 120	11,561 \pm 120	11,423 \pm 120	11,511 \pm 121
Pb, L_{α}	4821 \pm 88	4416 \pm 86	4123 \pm 83	4829 \pm 86	4433 \pm 86	4253 \pm 85
Pb, L_{β}	4068 \pm 91	3606 \pm 91	3409 \pm 85	3791 \pm 89	3756 \pm 90	3613 \pm 87

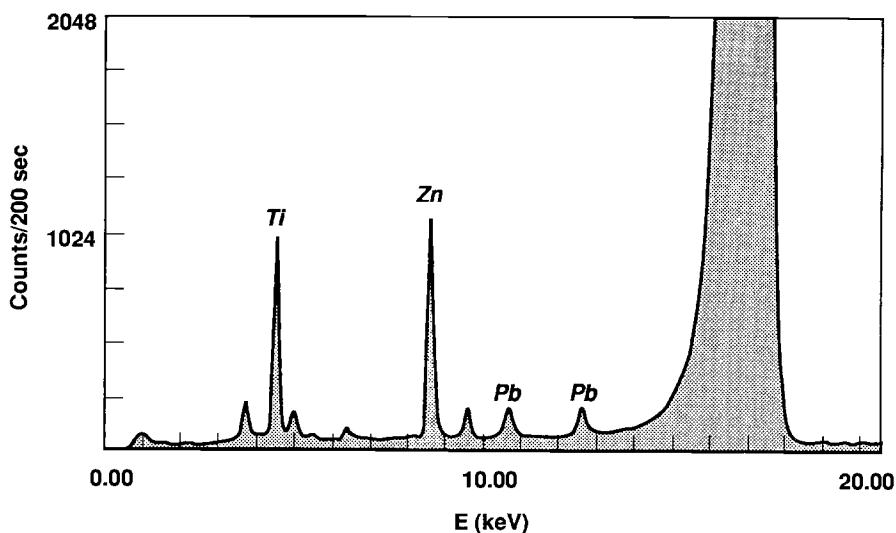


FIG. 3—XRF spectrum of a yellow bag typical for the second batch of bags.

difference between the two batches was very slight and a comparison based on visual examination could lead to errors. Even a measurement by a colorimeter will yield a small value for the absorption difference, accompanied by a large experimental uncertainty, due mainly to variations in thickness. Therefore, the confidence level of the colorimetric result will be low.

The XRF spectrum displayed in Fig. 3 is typical for the second batch of bags. The main and minor peaks were as in Fig. 2. The peaks' heights (and therefore areas) differed greatly between the two batches. The net peak areas (and their standard deviations) of the six bags of the second batch, evaluated for the main lines as described above, are given in Table 3. As in batch #1, the present batch (#2) shows reproducibility with respect to element concentrations.

The two batches were compared by calculating means for the six values of each XRF line and in each batch. The means and sample standard deviations are given in Table 4, as are the results of the statistical analysis of the means.

In this analysis, the significance of the deviation between the two means was tested by using the distribution of Student's t [4]. The parameter t is the deviation divided by its standard deviation. The standard deviation of t was calculated from the standard deviations of the two means added in quadrature. The probability p in Table 4 was

TABLE 3—Net XRF peak areas (\pm S.D.) in six bags—batch #2.

XRF Line	Y-7	Y-8	Y-9	Y-10	Y-11	Y-12
Ti, K_{α}	8735 \pm 109	8549 \pm 107	8668 \pm 107	7931 \pm 104	7964 \pm 105	8227 \pm 104
Zn, K_{α}	11,448 \pm 121	11,604 \pm 118	11,520 \pm 119	11,478 \pm 119	11,464 \pm 120	11,487 \pm 118
Pb, L_{α}	1653 \pm 64	1606 \pm 61	1781 \pm 61	1696 \pm 64	1731 \pm 62	1956 \pm 61
Pb, L_{β}	1358 \pm 75	1267 \pm 69	1518 \pm 67	1473 \pm 68	1512 \pm 69	1546 \pm 71

TABLE 4—Statistical analysis of mean peak areas (\pm S.D.) of XRF lines in two batches of yellow bags.

XRF Line	Mean Peak Area		<i>t</i>	<i>p</i>
	Batch #1 <i>n</i> ₁ = 6	Batch #2 <i>n</i> ₂ = 6		
Ti, K _α	5408 ± 172	8346 ± 355	18.24	5.26 × 10 ⁻⁹
Zn, K _α	11,551 ± 165	11,496 ± 62	0.7643	0.462
Pb, L _α	4479 ± 291	1737 ± 123	21.26	1.18 × 10 ⁻⁹
Pb, L _β	3707 ± 223	1446 ± 110	22.27	7.44 × 10 ⁻¹⁰

calculated for a random value falling outside the limits $\pm t$, for ν degrees of freedom. In the present calculation, $\nu = (n_1 - 1) + (n_2 - 1) = 10$.

The two batches differed significantly (that is, very low p value of the order of 10^{-8} to 10^{-9}) with respect to the peak areas of titanium and lead in the relevant pigments (Table 4). It is apparent that the intrabatch (sub-batch) variations of titanium and lead are much smaller than the inter-batch differences. On the other hand, the mean peak areas of zinc were significantly similar (that is, p of the order of 1). The nonsignificant difference between the two means of zinc was due to small chance variations in composition, sampling and counting. The overall finding from Table 4 can be interpreted by using a significance test. The null hypothesis in this case is that there are no differences between the two batches measured. The test statistic calculated in Table 4 reflects the deviation from the null hypothesis. If we chose a very cautious 0.1% level of significance, then the corresponding tabulated [4] value of t is 4.587, which is inferior to the computed value 18.24 for titanium or 21.26 and 22.27 for lead (see Table 4). Hence, the null hypothesis is disproved and the titanium and lead means of the two batches are not equal at the specified 0.1% level of significance. It should be noted that the null hypothesis is disproved at even lower levels of significance, for example, 10^{-4} to 5×10^{-9} .

The statistical analysis proved that even negligible differences of color in bags, which can be missed in a visual examination, or result in marked uncertainty in a colorimetric measurement, can be detected, identified and measured, at a very high level of confidence, by the XRF method.

The 12 samples, Y-1 to Y-6 in batch #1, and Y-7 to Y-12 in batch #2, were measured with a digital readout transmission densitometer (Macbeth, model TD-932). The spectral response of the instrument is in the visual, with repeatability of ± 0.01 . The mean optical densities were 0.527 ± 0.014 and 0.545 ± 0.008 for batch #1 and #2, respectively; errors are sample standard deviations. A major contribution to the dispersion of individual optical density results was the sensitivity to specimen thickness. In the statistical analysis of the means, we obtained $t = 2.734$ and $p = 0.0105$. Hence, the probability of an accidental matching of the two optical densitometric means is relatively high, 10^6 to 10^7 times greater than the probability calculated from the XRF results. The XRF analysis is therefore much more reliable than the colorimetric.

XRF spectra of green and blue bags are shown as examples for other colors. The spectrum of a green bag (see Fig. 4) shows the presence of the main peaks of titanium, iron, copper, lead and bromine. The blue bag (see Fig. 5) contains mainly calcium, titanium, copper and zinc. Testing of other, similar, green and blue bags, showed a significant variation in element composition. Our finding applies also to other colors and, similar to the case of yellow, which was treated in detail, enables the reliable sorting of colored bags, even those with similar colors, according to the element profiles.

Transparent polyethylene sleeves and bags (no pigment additives) of different origins, were examined in the XRF system. A typical spectrum of an Israeli-made polyethylene

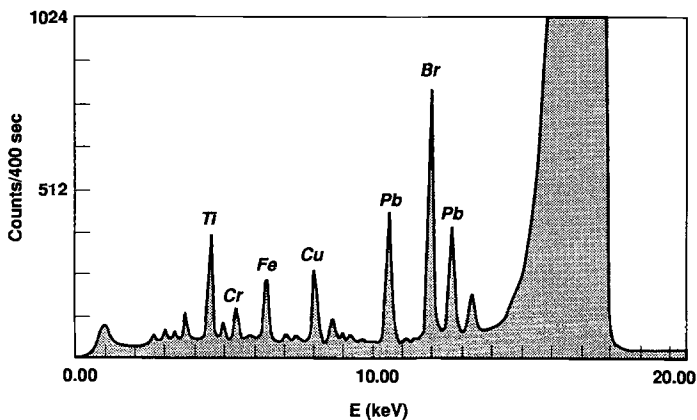


FIG. 4—XRF spectrum of a green bag.

is shown in Fig. 6. The peak heights are low, and are assigned to impurities—at the concentration levels of trace elements—in the polyethylene. In all brands, the main peaks are iron, copper and zinc. The ratios between the peaks' areas were found to be correlated with the origin of the polyethylene.

Absolute determination of element concentration by the 'standard addition' method was performed for zinc and lead. The latter element has an adverse significance as an environmental poison and the findings will be published elsewhere.

The concentration of zinc was measured in transparent polyethylene (no pigment additives). The calibration curve was established by pipetting 12.5 μ L to 37.5 μ L aliquots of a 100 ppm standard solution of zinc onto 10-mm-dia discs punched out of a polyethylene bag. The net peak area of the Zn K_{α} 8.64 keV XRF line was plotted against the mass of Zn deposited on the polyethylene disc (see Fig. 7). A straight line was fitted to the data by linear regression; the slope was 30,760 counts/ μ g Zn in a 500 s measurement; the correlation coefficient was 0.998. The net peak area of zinc in a 10-mm-dia disc of an Israeli-made polyethylene film (no standard addition) was 150 ± 25 counts in a 500 s measurement. Using the slope of the calibration curve (Fig. 7), the mass of zinc in the

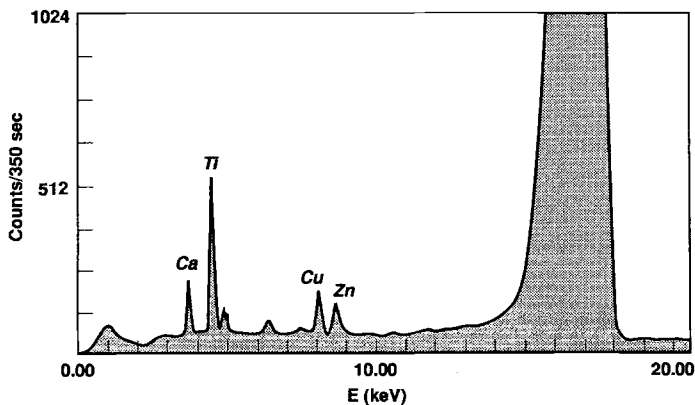


FIG. 5—XRF spectrum of a blue bag.

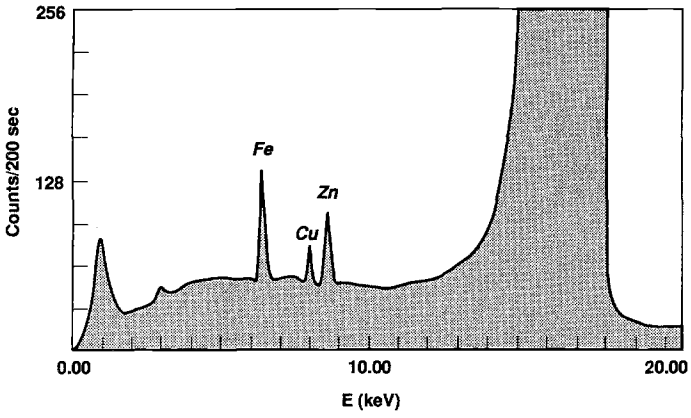


FIG. 6—XRF spectrum of an Israeli-made polyethylene.

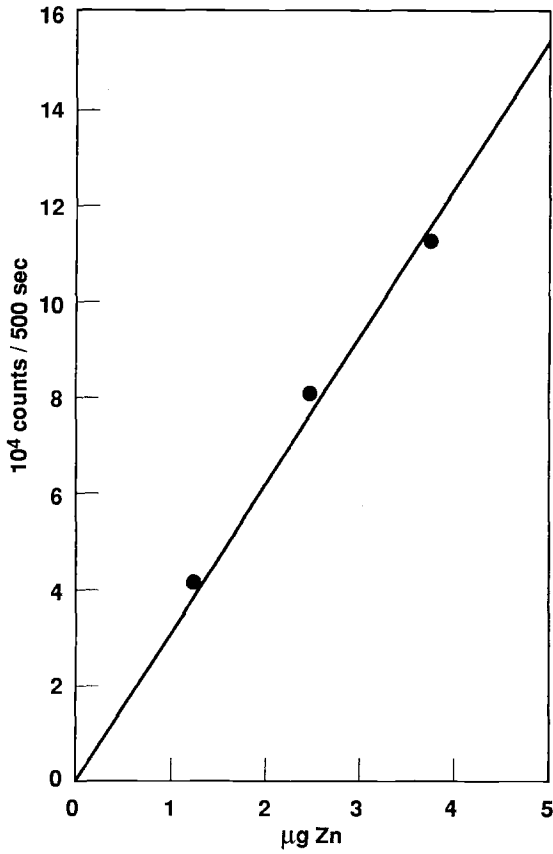


FIG. 7—XRF calibration curve for zinc.

disc was found to be 4.9 ± 0.8 ng. The mass of the disc was 8.0 mg and the concentration of zinc in the film was determined to be 0.6 ± 0.1 ppm.

The minimum detection limit (MDL) was calculated for zinc in this case using the expression [5] $MDL = 3.29 B^{1/2}/S$, where B is the background area under the zinc peak and S the sensitivity of the system at the prevailing experimental conditions. The sensitivity is given by the slope of the calibration curve. In the 500 s measurement, B was 1200 counts and the MDL was found to be 3.7 ng, or 0.46 ppm.

Conclusions

Colored polyethylene bags were shown to be homogeneous with respect to the distribution of inorganic pigments in the material. For XRF measurements, the locations of sampling in a suspect bag are therefore irrelevant. The XRF analysis is nondestructive and samples punched out from a bag can be re-measured and additional samples can be taken from the bag.

Batches of bags that differ very slightly in color, can be distinguished by the XRF analytical method at a very high level of confidence. Similar samples of colored polyethylene can be analyzed by colorimetry, but the uncertainty involved is very large, due to the small value of the differential measured and the relatively large associated experimental error.

The statistical analysis performed on the XRF results of two batches of very similar yellow bags, six bags in each batch, showed that the probability of an accidental matching is very low, of the order of 10^{-8} to 10^{-9} . This characteristic is explained by the fact that the deviation between the batches is many times greater than the internal variation of any batch.

On the other hand, the question of attributing a bag to its correct batch can be dealt with in principle by comparing two groups—six samples from the suspected bag and six bags from the batch. By using the results for zinc in the two yellow batches, it may be inferred that a null hypothesis concerning the questioned bag will not be disproved at a significance level of approximately 50%.

Element profiles of colored polyethylene bags, as analyzed in this work, can be used in discriminating between a piece cut from a colored polyethylene bag, and a batch of bags, where the aim is to determine, at a high level of confidence, the common origin of the cut piece and the batch. Such discrimination has a significant application in forensic examinations of colored polyethylene bags, often used in criminal activities associated with drugs.

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References

- [1] Cleverley, B., "The Comparison and Matching of Low Density Polyethylene Plastic Bags by Infrared Spectroscopy," *Journal of Forensic Sciences*, Vol. 24, No. 2, April 1979, pp. 339–345.
- [2] Von Bremen, U. G. and Blunt, L. K. R., "Physical Comparison of Plastic Garbage Bags and Sandwich Bags," *Journal of Forensic Sciences*, Vol. 28, No. 3, July 1983, pp. 644–654.
- [3] Stone, R. S., "The Examination and Comparison of Plastic Bags Used in Home Heat Sealers," *AFTE (Association of Firearms and Toolmarks Examiners) Journal*, Vol. 18, No. 1, January 1986, pp. 21–23.

- [4] Fisher, R. A. and Yates, F., *Statistical Tables for Biological, Agricultural and Medical Research*. 6th ed., Oliver and Boyd, London, England, 1963.
- [5] Currie, L. A., "Limits for Qualitative Detection and Quantitative Determination—Application to Radiochemistry." *Analytical Chemistry*. Vol. 40, No. 3, March 1968, pp. 586–593.

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