CASE REPORT

Myriam Azoury,[1] *M.Sc. and Nadav Levin,*[1] *M.Sc.*

Identification of Zinc Phosphide in a Falsely Labeled Rodenticide Bait

REFERENCE: Azoury M, Levin N. Identification of zinc phosphide in a falsely labeled rodenticide bait. J Forensic Sci 1998; 43(3):693–695.

ABSTRACT: ''Kela'' is a commercial rodenticide bait commonly used in Israel, made of wheat grains, which, according to its label, contains chlorophacinone. This product was involved in the death case of a man in which the victim's female companion was accused of assisting in this suicide and was subsequently convicted. Analysis of the wheat grains revealed zinc phosphide, whose use is restricted to authorized exterminators only, instead of chlorophacinone. Zinc phosphide was identified using microscopic examination, scanning electron microscopy/energy dispersive X-ray spectroscopy (SEM/EDX) and X-ray powder diffraction (XRD).

KEYWORDS: forensic science, zinc phosphide, chlorophacinone, poisoning, suicide, trace evidence

Identification of unknown compounds in the Division of Identification and Forensic Science (DIFS) of the Israeli Police is usually performed by two laboratories. The Analytical Chemistry Laboratory analyzes organic substances and the Toolmarks and Materials Laboratory analyzes mainly inorganic substances. As the majority of commercial pesticides contains active organic ingredients, they are first submitted for analysis to the Analytical Chemistry Laboratory, and later, if necessary, they are transferred to the Toolmarks and Materials Laboratory. We present here a case in which a commercial pesticide bait, claimed to contain chlorophacinone, an organic pesticide, was found to contain, instead, zinc phosphide, an inorganic pesticide.

Case History

In 1991, a sixty-seven-year-old man with a past history of multiple suicide attempts, was found unconscious in his apartment in Hertzlya, Israel. He was transferred to the hospital but died 12 hours later. Due to a suspected poisoning, postmortem examinations were performed at the Institute of Legal Medicine. The autopsy examination revealed a large quantity of wheat grains in the victim's stomach. However, toxicological analyses of the blood and urine gave no indication of the presence of drug or poison, apart from benzodiazepines and their metabolites.[2] Search of the victim's apartment led to the discovery of a few gray-black wheat grains suspected to contain pesticide. Further inquiry revealed that the victim's female companion had purchased a commercial rodenticide named ''Kela'' at a local pharmacy. She claimed that she had purchased the rodenticide at the victim's request and that he used it to execute the suicide. Prior to the exhibit's analysis, in the course of the investigation, the investigators were requested by the authors to purchase a similar ''Kela'' package at the same pharmacy. This was transferred to the Analytical Chemistry Laboratory together with the few gray-black wheat grains collected from the victim's apartment (Fig. 1).

According to the label information, the ''Kela'' baits contain 0.0075% chlorophacinone (Fig. 2). Chlorophacinone is a registered anticoagulant rodenticide having 50% mortality acute oral lethal dosages (LD_{50}) of 20.5 mg/kg for rats (1, p. 302).

Instrumentation and Analytical Procedures

The analyses in the Analytical Chemistry Laboratory were carried out using Finnigan TSQ 700 direct inlet mass spectrometry. Temperatures were programmed from 40°C to 290°C at 25°C deg/min. Scan range was 1 scan per second and electron energy was 70 eV.

The analyses in the Toolmarks and Materials Laboratory were done using a CamScan 4 scanning electron microscope, equipped with a Tracor Northern TN 5500 X-ray analyzer (SEM/EDX), and a Diano X-ray powder diffraction (XRD) system. Samples for SEM/EDX analysis were mounted on aluminum stubs, coated with 3M 465 double-side adhesive, and carbon-coated. The analyses were performed using accelerating voltage of 25KV. XRD analysis was carried out on samples mounted on glass slides coated with the above-mentioned double-side adhesive. Copper (Cu) radiation was used. The tube current was 25 mAmps and the accelerating voltage was 40KV. The 2Θ range was 5°–90° and the scan rate was 2°/min.

Methodology and Discussion

First, based on the label information, standard analytical procedures were performed in the Analytical Chemistry Laboratory to identify chlorophacinone in the purchased bait. These procedures included grinding the wheat grains, then extracting the ground

[1]Deputy Head, Analytical Chemistry Laboratory, and Head, Toolmarks and Materials Laboratory, respectively, Division of Identification & Forensic Science, Israel Police National Headquarters, Jerusalem.

Received 9 April 1997; and in revised form 15 Sept. 1997; accepted 15 Sept. 1997.

[2]Based on trial transcripts.

FIG. 1—*A sample of the ''Kela'' rodenticide bait, made of wheat grains with gray-black powder on the surface.*

FIG. 2—*Labeled package of the ''Kela'' rodenticide: ''Ministry permit number'' (in Hebrew) 062/2/65 appears on the label.*

grains with dichloromethane and analyzing the extract by direct inlet mass spectrometry. In spite of many attempts, neither chlorophacinone nor any other organic pesticide could be detected, despite the fact that chlorophacinone standard could be detected using the same analytical method. Additional ''Kela'' packages were purchased by the authors in different pharmacies, but in no case was chlorophacinone detected using our standard procedures. One could assume from these results that the concentration of chlorophacinone in the wheat grains was too low and therefore undetectable by our instruments. Despite this fact, the woman was indicted and was accused of assisting in a suicide.

About 18 months later, another case was investigated in which gray-black wheat grains were submitted to the Analytical Chemistry Laboratory. The metallic appearance of the wheat grains and their gray-black color suggested the possibility that they could contain zinc phosphide, an inorganic pesticide powder previously submitted in several cases and analyzed by the DIFS laboratories. Therefore the exhibits were transferred to the Toolmarks and Materials Laboratory. The gray-black particles on the wheat grains were indeed identified as zinc phosphide. Zinc phosphide is also a rodenticide, having 50% mortality acute oral lethal dosages (LD_{50}) of 40.5–46.7 mg/kg for rats (1, p. 1457).

The authors noticed the similarity in appearance between these baits and those submitted in the past in the above reported suicide case, and raised the possibility that the label information on the ''Kela'' packages was incorrect. Therefore a new aliquot of ''Kela'' baits, kept in the pesticide collection of the DIFS was also submitted to the Toolmarks and Materials Laboratory. Zinc phosphide was identified on the ''Kela'' baits. Although a long time had elapsed and the trial had already begun, the remaining exhibits of the suicide case were resubmitted to the DIFS laboratories for analysis. Only two gray-black wheat grains which had been collected from the victim's apartment remained and were available for analysis.

As a standard routine in the Toolmarks and Material Laboratory, the exhibits were examined using a low magnification stereomicroscope ($\times 60$). Gray-black particles with metallic luster were observed on the two wheat grains and were similar to those observed on the ''Kela'' wheat grains. The gray-black particles were then subjected to SEM/EDX analysis. The analyses were performed on the wheat grains collected from the victim's apartment as well as on those purchased at the pharmacy. As seen in Fig. 3, zinc and phosphorus were detected on the gray-black particles collected from all the wheat grains analyzed.

The gray-black particles collected from the ''Kela'' wheat grains were also analyzed by XRD. Zinc phosphide was identified. Because of the small amount of particles on the wheat grains collected in the victim's apartment, XRD analysis was not performed on them. Nevertheless, based on the literature (2), there is no other material having the same chemical composition, color and metallic luster as zinc phosphide.

The authors were then requested by the prosecutor to perform an approximate quantitative analysis of the pesticide in the ''Kela'' package. It was found that each package (weighing about 90 g) contains about 1500 wheat grains. In order to remove the gray-black zinc phosphide particles from the grains, known numbers of wheat grains were rolled on glass slides coated with double-side adhesive. The weight of the zinc phosphide, collected on each slide, was then determined. It was found that the estimated zinc phosphide weight in each ''Kela'' package is about 1 g, less than 1 mg on each wheat grain.

The analyses performed provided evidence that the pesticide on the ''Kela'' product was zinc phosphide and not chlorophacinone, as cited on the package. In addition we could establish to a high degree of certainty that the compound on the wheat grains found in the victim's apartment was also zinc phosphide.

These findings were transferred to the Ministry of Health. Consequently, the Ministry forbade the sale of this product, which was not only falsely labeled, but also falsely claimed to have a Ministry

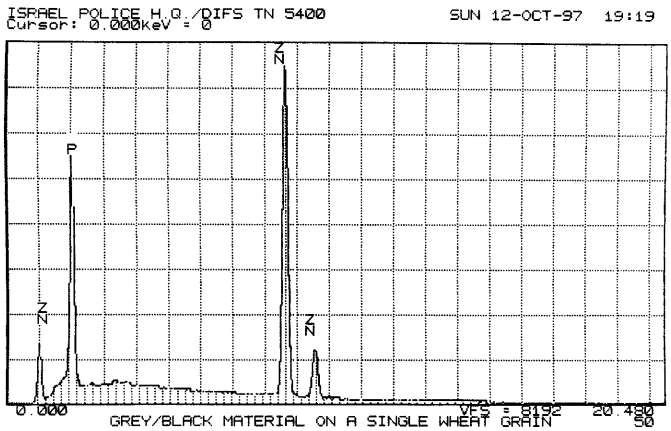

FIG. 3—*SEM/EDX spectrum of gray-black particles collected from the ''Kela'' wheat grains.*

permit. A regulation of the Ministry forbids the use of zinc phosphide in Israel by anyone other than an authorized exterminator. The victim's companion was found guilty of assisting in a suicide.

Conclusions

The analysis performed on the ''Kela'' bait provided evidence that zinc phosphide, instead of chlorophacinone as cited on the label, was added to the wheat grains. Analysis procedures used in the Toolmarks and Materials Laboratory enabled the identification of the pesticide on an exhibit as small as one wheat grain, with no need for chemical extraction, as usually performed on pesticide exhibits.

References

1. Windholz M, Budavari S, Blumetti RF, Otterbein ES, editors. The Merck Index, 10th Edition. Merck & Co., Inc., 1983.
2. Weast RC, editor. CRC Handbook of Chemistry and Physics, 1st Student Edition, CRC Press Inc., 1987.

Additional information and reprint requests:
Myriam Azoury
Analytical Chemistry Laboratory
Division of Identification & Forensic Science
Israel Police National Headquarters
91906 Jerusalem, Israel