TECHNICAL NOTE

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Differentiation of Automotive and Locomotive Lubricant Oil

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ABSTRACT: Migratory waterfowl can confuse open oil pits for freshwater ponds. These open pits lead to waterfowl death. Frequently the pits contain oil and waste lubricant oil from automotive or locomotive origin. Automotive lubricant oil contains zinc dithiophosphate, a detergent and dispersant chemical additive. Locomotive lubricant oils do not contain zinc dithiophosphate. A GC-MS and XRF technique is presented that allows for the characterization of used lubricant oil as to being from automotive of locomotive sources. Identification of the oil source aids in the prosecution of open oil pit owners.

KEYWORDS: forensic science, lubricant oil, automotive, locomotive, XRF, waterfowl

Migratory waterfowl can confuse open oil pits for freshwater ponds. Landing in such pits can lead to death by hypothermia and poisoning by ingestion, inhalation, and overall oil toxicosis [*1*]. Locomotive engines contain between 150 to 200 gallons of oil. When the oil is changed it is sometimes discarded in large pits. Similarly, many rural areas have oil pits were farmers discard used lubricating oil from cars, trucks and other farm engines.

Producers of waste oil have rigorous guidelines with which they must comply. By law waste oil producers are required to cover their pits with netting to prevent the accidental death of migratory birds. When dead waterfowl are found in or associated with unprotected pits wildlife law enforcement personnel must determine the source of the oil in order to prosecute the violators. Many papers have been published concerning the identification of oil or oil pollutants [*2*]. Characterization has been done by gas chromatography [*3,4*], infrared analysis [*3,5*] fluorescence spectroscopy [*3,6*], high pressure liquid chromatography [*3*], emission spectroscopy [*7*], and gas chromatography mass spectrometry (GC-MS) [*8*]. Trace elements have been used to infer engine metal wear or soil

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contamination from lubricating oil [*14*]. Forensic individualization of lubricant oils has been accomplished by Yit [*17*] using column chromatography followed by infrared analysis, and Kubic [*9,10*] has attempted individualization of lubricant oils by variable separation synchronous excitation fluorescence.

The National Fish and Wildlife Forensic Laboratory has developed a technique which differentiates between automotive and locomotive lubricant oil based on the presence of zinc dialkyldithiophosphates, an oil dispersant.

Zinc dialkyldithiophosphates (Fig. 1) is an additive to automotive lubricant oil. It is used as a detergent and dispersant whose function is to prevent engine rust and corrosion from forming sludge or varnish deposits. This detergent keeps combustion byproducts finely suspended and it minimizes deposits [*12*]. Selected marine, aviation and locomotive engines, particularly diesel engines by General Electric Company and Electromotive Division of General Motors are manufactured with engines that contain silver. Zinc is corrosive to silver and therefore locomotive engines oils do not contain zinc dialkyldithiophosphates. All crude oil and fuel oils contain a considerable number of trace metallic elements ranging quantitatively from ppb to ppm [*13,7*]. Zinc is rarely found in crude oils. When it is detected it is found as a trace contaminant [*13,7*].

Materials

Quantitative oil standards were prepared from an oil based 5000 ppm Zinc (weight) standard (Conostan Metallo-Organic Standards) and a paraffinic hydrocarbon oil (Conostan 20 Base oil) with a 17 cSt viscosity (40°C). Zinc free base oil was used to bring the oil content of the blank, standard and sample solutions to equivalent viscosity. Reagent grade methyl-isobutyl ketone (MIBK) and hexane were purchased from Mallinckrodt Inc., Automotive oil (Table 1) was purchased from local sources. Locomotive oil (Table 1) were obtained courtesy of Exxon Company and Amoco Oil Company.

Oil species (light fuel, heavy fuel or lubricant oil) were identified on a HP 5890 Gas chromatograph coupled to a HP 5988A Mass Spectrometer. Five microliters of sample were analyzed on a J&W DB-5 column (30 m × 0.32 mm i.d. × and 0.1 μm film). Oven conditions were 60°C to 280°C at 3°C/min and held at 280°C for 30 min. Injection port was kept at 250°C.

Unprocessed oil samples were qualitatively analyzed on an Asoma (Baird) EX-6000 x-ray fluorescence spectrometer (XRF) equipped with a rhodium tube and operated with 40 kV at 100 μA. Dead time was kept between 30% and 50%.

Quantitative data was collected on an Instrumentations Laboratory 151 Atomic Absorption (AA)/Atomic Emission Spectrophotometer equipped with a Hamamatsu Cu/Cd/

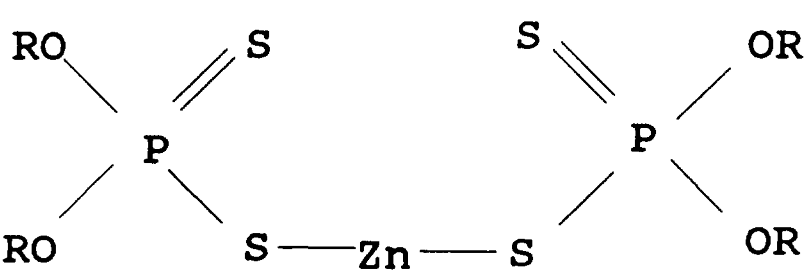

FIG. 1—*Zinc dialkyldithiophosphates. Isomers for the R groups can range from C_3 to C_{12} or benzene.*

TABLE 1—*Presence of zinc in various lubricating oils by X-ray fluorescence and atomic absorption analysis.*

Oil source	Industry use	ZN Present by XRF?	AA Quantitative results (PPM)
Exxon diol 2211	Locomotive	NO	<20
Exxon diol 2212	Locomotive	NO	<20
Exxon diol 2213	Locomotive	NO	<20
Exxon diol 2219	Locomotive	NO	<20
Exxon diol 2211	Locomotive	NO	<20
Amoco super 13	Locomotive	NO	<20
Chevron delo 15w-40	Automotive	YES	1670
Valvoline 10w-40	Automotive	YES	1650
Havoline, 10w-40, formula 3	Automotive	YES	1670
Quaker State 10w-40	Automotive	YES	1630
Penzoil, 10w-40	Automotive	YES	1480
Western Family, 10w-40	Automotive	YES	1360
Gear, 85–140 wt	Automotive	NO	<20
Airplane Oil	Aviation	NO	<20

Zn/Pd hallow cathode source tube, operating in the atomic absorption mode at 213.55 nm and slit width of 320 μm. with an acetylene/air flame.

Methods

Aliquot samples of questioned oil were prepared for GC-MS analysis by adding 1 mL of oil to 9 mL of hexane. XRF analysis of questioned samples was performed by transferring 3 mL of undiluted oil to a 1 inch diameter sample cup with a polypropylene film base.

AA analysis followed the ASTM D4628 [*11*]. Working standards for AA were prepared by weighing 0.0206, 0.0656, 0.0911 and 0.1234 g of the 5000 ppm zinc (wt) standard into 100 mL volumetric flasks. Base oil was added to each so that a weight of 0.4 g was achieved. Standards were then diluted to 100 mL with MIBK. The empirical lower detection limit of this assay was 20 μg/g. All AA analytical samples were prepared by weighing 0.1231 g of the oil into a 50 mL volumetric flask. The weight was brought to 0.2 g with base oil and the sample was diluted to 50 mL with MIBK.

Results and Discussion

In the present work, GC-MS analysis was used to characterize the type of petroleum product (light fuel, heavy fuel and lubricating oil) by determination of the paraffin elution profile [2]. Light fuel oils elute in the described method in the range of 60 to 200°C, heavy fuel oils elute at 150 to 250°C, and lubricating oils elute at 200 to 280°C.

XRF was used to qualitatively determine the elemental composition in common commercial automotive and locomotive lubricating oils. XRF analysis indicated that zinc was detected in all of the automotive oils but not in locomotive lubricant oils (Table 1). Atomic Absorption analysis of these automotive and locomotive lubricating oils indicated that automotive oils contained between 1130 μg/g and 1679 μg/g (ppm) of zinc whereas zinc was not detected in any of the locomotive lubricating oils (Table 1).

The lack of zinc in the locomotive oils is in agreement with the commercial literature [*15,16*]. It is of interest to note that one sample of gear oil (85–140 wt) and one unknown sample of used airplane motor oil did not contain zinc. The quantity of used gear and airplane oil is negligible when compared to locomotive sources. In a case example, evidence waterfowl carcasses were received and diagnosed with death due to oil toxicosis. Hexane extraction of oiled feathers were analyzed by GC-MS and XRF. GC-MS analysis revealed that the samples were consistent with lubricating oil. The absence of zinc by XRF analysis and the geographical location of the carcasses indicated that the samples were consistent with locomotive lubricating oil.

Conclusion

Automotive motor oils contain zinc dialkyldithiophosphates, an additive to engine lubricant oil. This additive gives these motor oils an inference of its source since locomotive, marine and some aviation lubricant oils do not contain zinc dialkyldithiophosphates. Determination that an oil is a lubricant can be accomplished by GC-MS. Automotive source inference of a lubricant oil can easily be accomplished by XRF.

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