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Trace metal determination by total-reflection X-ray fluorescence (TXRF) for the differentiation between pure fuel oil (bunker oil) and waste oil (sludge) in maritime shipping legal cases

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Abstract—Using a simple sample preparation technique, the concentrations of Ca, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn and Pb in several bunker and sludge oils have been measured simultaneously by total-reflection X-ray fluorescence analysis (TXRF) in the mg/kg range. As a result, five elements are suitable in distinguishing between both types of oil: Ca, V, Fe, Ni and Zn. This differentiation can be used in cases where shipping vessel captains or chiefs attempt to conceal illegal waste oil discharge at sea by wrongly declaring bunker oil as sludge.

1. INTRODUCTION

To PROSECUTE offenders of the MARPOL Convention (International Convention for the Prevention of Pollution from Ships, 1973, as modified by the Protocol of 1978 [1]), examinations of the whereabouts of waste oil are increasingly carried out in harbours by the water police.

The lack of sludge strongly implies non-compliance with the MARPOL Convention because, by implication, oil residues must have been discharged at sea. An increasing number of cases have been recorded where pure fuel oil (bunker oil) has been declared as sludge by chiefs or captains of shipping vessels to avoid being accused of such an offence. In other cases, it was maintained that the missing volume of sludge was added to bunker oil. Proving this statement requires methods of distinguishing bunker and sludge oil.

Fuel oil contains vanadium and nickel that originates from natural geological sources. These two elements are dissolved in the matrix. Furthermore, fuel oil contains particulate and metalliferous, incombustible components that have to be separated before combustion in the ship's engine. During this refining process (Fig. 1), suspended

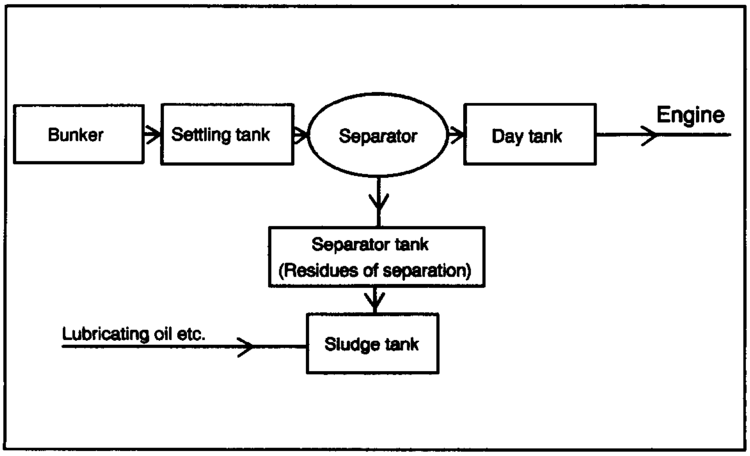


Fig. 1. Scheme of the ship fuel oil refining process.

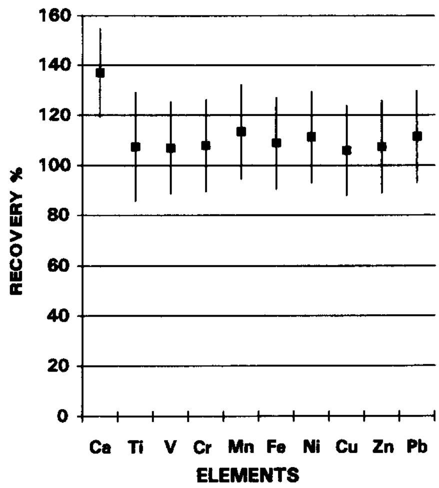


Fig. 2. Recoveries and relative standard deviations of the multielement standard oil S-21 (CONOSTAN), measured by TXRF ($n = 5$).

components are separated and accumulated in the waste oil (sludge) together with metalliferous particles from artificial sources (e.g. metal abrasion).

The amounts of loaded and consumed oil have to be registered in the oil record book. Under working conditions, at least 1% of the consumed oil results as sludge. The regular discharge of sludge in harbours must be proven by a registration in the ship's oil record book. Two cases require an investigation.

(1) There is no proof for the regular discharge of a missing sludge volume. It is claimed that the sludge had been fed back into the bunker tank—with the consequence that refining is done to no purpose. In this instance, increased metal concentrations in the bunker tank have to be determined in relation to the mixed volume of bunker and sludge.

(2) Captain and chief are suspected to have replaced illegally discharged sludge with bunker oil. In these instances, the bunker and sludge tank contain the same oil with the characteristic metal contents as are found in bunker oil.

In former times, analysis of organic oil components was used for the identification of bunker and sludge oil [2,3]. Yet, in some circumstances, this method was not sufficiently unequivocal in determining the oil type. However, as is shown in various works using classical X-ray fluorescence analysis, the metal content of fuel and waste oil is suitably discriminated for different types of oil [4–7]. The TXRF provides an efficient way for the multiple analysis of elements with low detection limits in combination with a simple calibration and sample preparation procedure.

2. EXPERIMENTAL

2.1. *Apparatus*

The TXRF spectrometer consists of an EXTRA II module (Rich. Seifert, D-2070 Ahrensburg) with single beam excitation (molybdenum tube), an X-ray generator, a Si(Li) detector, an automatic sample changer and a computer controlled multichannel analyser system (Link Systems AN 10000).

Table 1. Detection limits (3 times standard deviation of the blank) of oil, measured by TXRF (mg/kg)

Ca	Ti	V	Cr	Mn	Fe	Ni	Cu	Zn	Pb
16.65	3.43	6.53	2.49	5.01	11.65	4.78	2.48	4.44	4.73

Table 2. Metal concentrations in pure fuel (bunker) oil. Thirty-four bunker oils were measured. Some ships were sampled repeatedly at different times

Ship no.	Ca (mg/kg)	Ti (mg/kg)	V (mg/kg)	Cr (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/kg)
1	98	<41	138	<17	<13	142	65	6	9	<30
2	44	<16	242	<8	<5	57	90	<3	<2	<12
3	51	24	371	<10	<6	56	78	<3	7	<15
4	35	<26	138	<11	<9	65	49	<5	<4	<21
5	35	32	63	<12	<9	106	30	<4	<4	<21
6	<37	<27	241	<13	<9	83	92	<5	<4	<21
7	27	<16	216	<8	<5	54	83	<3	4	<13
8	37	<25	253	<12	<8	53	85	<4	<4	<18
9	<27	<20	229	<9	<7	67	83	<3	<3	<16
10	49	<34	253	<16	<11	50	96	<5	<5	<25
11	<130	<96	340	<43	<31	175	145	<14	<14	<71
12	<27	<21	233	<10	<7	46	89	<3	<3	<16
13	132	19	118	<8	<6	46	45	5	29	<14
13	99	<10	149	<4	<3	43	36	2	36	15
14	285	<36	235	<16	<11	70	102	<6	<5	33
14	<50	<39	134	<18	<12	44	44	<6	<6	<29
15	21	<17	248	<8	n.d.	45	86	<3	<3	<12
15	<29	23	147	<10	<7	66	64	<4	<3	<17
16	235	20	247	<6	<4	47	98	<2	2	10
16	<18	<14	258	<7	n.d.	40	97	2	n.d.	12
16	34	<21	225	n.d.	n.d.	65	82	4	<3	<16
17	<24	n.d.	109	n.d.	<6	40	44	58	4	<14
17	<27	<21	87	<9	<7	29	67	n.d.	<3	<16
18	80	<37	674	<18	<11	99	93	<6	18	31
18	<55	<43	239	<19	<13	165	77	<7	<6	<30
19	<40	<30	319	<14	<10	88	123	<5	<4	23
20	632	<97	325	n.d.	<31	378	109	<16	31	90
20	<42	<33	199	<14	<10	45	72	<5	<5	<22
21	<24	36	182	<9	<6	81	<66	4	3	<14
22	<19	<15	68	<6	<5	26	64	<2	<2	12
22	47	<29	118	n.d.	<10	49	34	<5	<4	<22
23	15	< 9	168	<4	<3	38	56	<1	<2	<7
23	<21	<16	217	<7	n.d.	82	75	<3	3	<12
24	113	<191	154	<9	n.d.	105	87	5	61	27

2.2. *Sampling*

Figure 1 shows a scheme for fuel oil refining in ships. The separator removes the incombustible components that are initially stored in the separator tank and then fed into the sludge tank, together with other waste oils such as used lubricating oil etc. Samples were removed from the bunker and sludge tanks and stored in glass bottles. Sampling, at that time for the analysis of organic compounds, was carried out between September 1988 and November 1989.

2.3. *Sample preparation*

An oil sample (3–10 mg) was diluted with 1 ml of toluene that was pre-cleaned by sub-boiling distillation. For internal standardization, an appropriate amount of Ga in organic solution was added (e.g. 1000 mg/kg) [8]. One microlitre of the sample, prepared in this way, was dried on a silica sample carrier. For the preparation of the blank, the oil sample was substituted for a similar amount of base oil and also dried on a silica sample carrier.

3. RESULTS

3.1. *Standard material measurements*

For measuring the accuracy and standard deviation, a multielement standard oil (CONOSTAN Metallo Organic Standard S-21: nominal value 900 mg/kg for each element) was analysed. All recoveries, except for Ca, amount to 107–113%. Calcium

Table 3. Metal concentrations in waste (sludge) oil. Twenty-nine sludge oils were measured. Some ships were sampled repeatedly at different times

Ship no.	Ca (mg/kg)	Ti (mg/kg)	V (mg/kg)	Cr (mg/kg)	Mn (mg/kg)	Fe (mg/kg)	Ni (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	Pb (mg/Kg)
1	1494	17	56	44	11	1969	24	19	221	34
2	2400	<21	74	17	9	764	41	<3	170	18
3	364	<21	151	<9	<7	39	31	<3	22	16
4	7770	<18	81	<8	7	750	31	12	154	15
5	9846	40	92	<9	31	591	66	7	77	28
6	89	<14	147	<6	<4	246	56	3	18	14
7	7092	<25	98	<11	<8	775	49	7	101	25
8	3816	<8	72	4	<3	464	20	7	161	10
9	1117	25	97	<8	11	1456	40	8	90	19
10	1695	12	114	37	8	665	45	11	265	12
11	9041	<15	163	12	7	522	55	13	293	18
12	2645	<32	186	<14	<10	1029	77	12	180	23
13	1702	75	54	13	26	6738	36	23	163	65
14	4285	14	53	<6	<5	477	23	3	277	<6
14	2848	<10	40	<4	<3	101	19	<2	<352	<9
15	1481	<21	83	<9	<7	215	36	<3	170	17
15	2622	<27	78	<12	<9	288	36	<5	158	<20
16	5164	73	362	25	11	4222	150	73	382	56
16	1295	<20	154	<9	<7	476	83	6	41	15
17	4161	30	124	22	14	1858	52	24	191	30
17	963	21	88	28	11	1358	58	11	111	25
18	2108	14	121	<4	4	781	30	10	138	28
19	1164	<17	177	<8	8	133	61	<3	17	13
20	2915	<21	93	<9	<7	183	43	5	467	<15
20	3505	45	132	<17	<12	1114	58	45	503	72
22	329	<27	188	<12	<9	218	44	7	13	<19
22	132	80	123	n.d.	<15	1094	170	8	24	<31
23	551	<16	220	n.d.	<5	278	68	11	23	<12
23	1049	<17	199	<8	<6	444	79	15	47	16

achieves a recovery of up to 137% (Fig. 2). The relative standard deviations (precision within series) of all elements were found to be 18%, except for Ti with 22%. The precision of measurement was found to be between 0.3 and 0.8%.

Recoveries higher than 100% might be explained by the evaporation of volatile components during storage.

3.2. *Detection limits*

The detection limits (3 times standard deviation of the blank) were determined from measurements of five toluene-diluted base oil samples. Results are given in Table 1.

3.3. *Bunker and sludge oil measurements*

Searching for characteristic differences in element concentrations of pure and waste oils, we analysed 34 bunker and 29 sludge oil samples from 24 different ships. The results are shown in Tables 2 and 3.

The spectra (Fig. 3) show the typical patterns of fuel and waste oil. Five elements are suitable in distinguishing between the two types of oil: Ca, V, Fe, Ni and Zn.

4. DISCUSSION

A distinction between sludge and bunker oil is relatively easy to obtain if both types of oil are available from the same batch (same time, same ship). Higher concentrations of calcium, iron and zinc characterize sludge oil. Higher concentrations of vanadium and nickel usually characterize bunker oil. A small number of our analyses of bunker oils (six samples), however, showed *lower* vanadium and nickel concentrations than

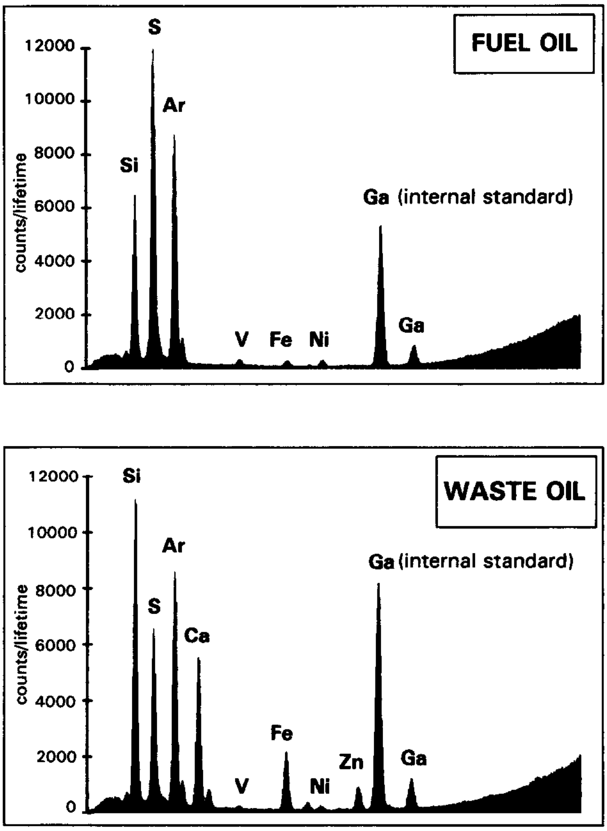


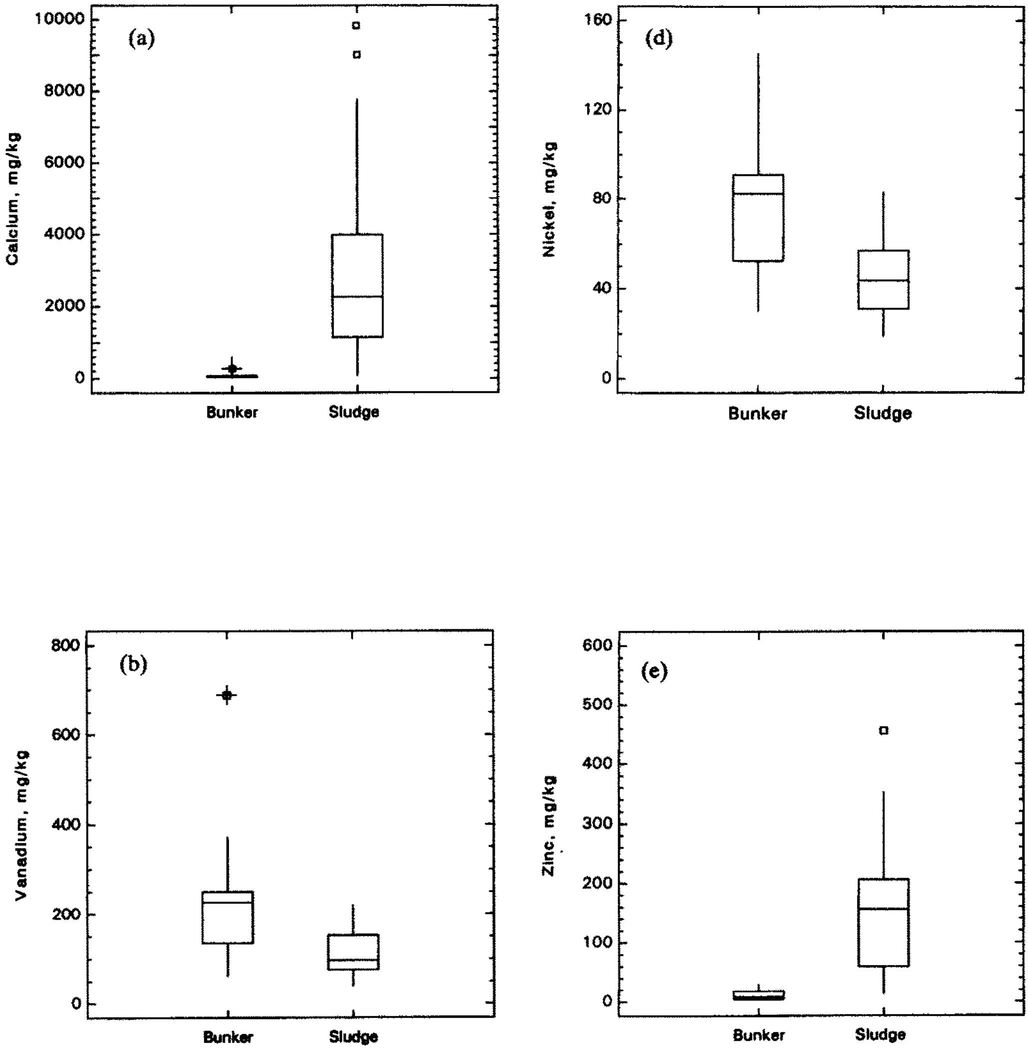
Fig. 3. TXRF spectra of a fuel (bunker) oil and a waste (sludge) oil sample. Aquisition time: 1000 s.

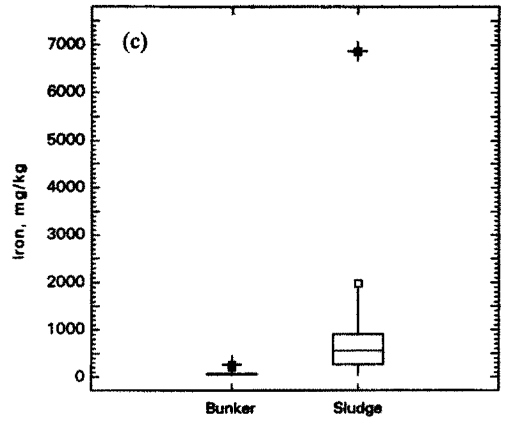
in the corresponding sludge. Nevertheless, their calcium, iron and zinc concentrations were distinctly lower than those found in sludge oil thus confirming the characteristic of bunker oil.

A much more difficult task is to identify an isolated bunker or sludge oil sample. To identify oil as sludge with a high probability, the concentrations of calcium, iron and zinc must be significantly higher than the maximum concentrations that can occur in bunker oil (Fig. 4(a)–(e)). If low concentrations of these three elements are found in a sample, it may either be legitimately bunker oil or a sludge oil. The relative contribution of vanadium and nickel then provide an additional way of identification.

Normalizing the sum of the concentrations of the five main components to 100%, we get two different patterns for bunker and sludge. As shown in Fig. 5(a) and (b), the main trace element component of bunker oil is vanadium. The percentage of nickel is the same order of magnitude as that of calcium and iron. In contrast, the main component of sludge oil is either calcium or iron (in exceptional cases Zn), but never vanadium. The percentage of nickel does not reach the level of calcium and iron. The examples shown in Fig. 5(a) and (b) are easy to interpret.

Another example (Fig. 6(a)) shows a less obvious pattern. In this instance, calcium is the main component with iron and zinc also present at relatively high levels. If only this oil should be available, one may hesitate to identify it as bunker oil as declared. Only the comparison with the corresponding sample from the sludge tank (Fig. 6(b)) proves such a declaration to be true.





The box and whisker plot divides the data into four areas of equal frequency. The box covers the middle 50 per cent of data values between the lower and the upper quartile (each 25 per cent of the data values). The median is drawn as a vertical line inside the box. The whiskers extend out to the smallest (largest) data point within the 1.5 interquartile range. Points between 1.5 and 3.0 interquartile ranges appear as small open boxes. A point beyond 3.0 interquartile ranges appears as a dot.

Fig. 4. Box and whisker plots of the metal content in pure fuel (bunker) oils and waste (sludge) oils (n = 24). Only corresponding pairs of bunker and sludge samples have been included in the diagram.

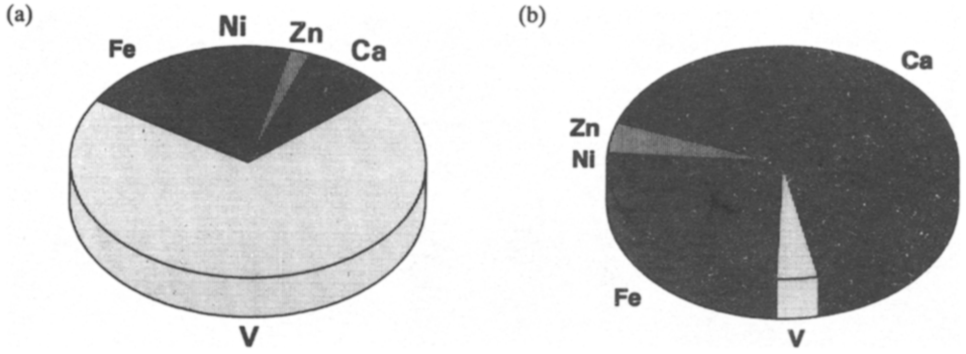


Fig. 5. Example of a typical metal composition found in (a) bunker and (b) sludge oil. The sum of the concentrations of Ca, V, Fe, Ni and Zn has been normalized to 100%.

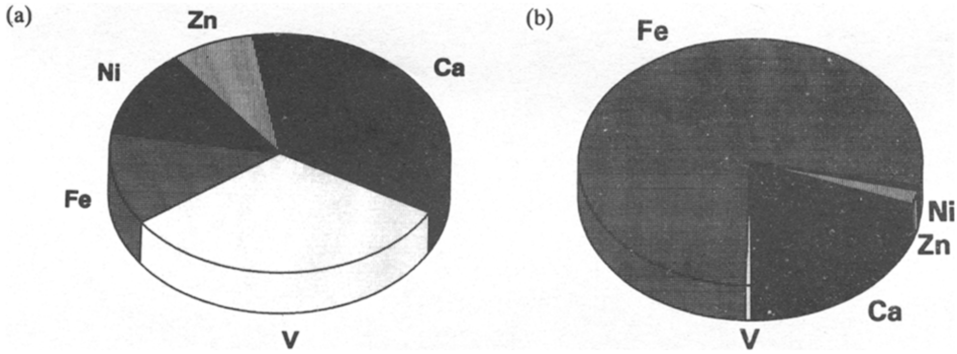


Fig. 6. Example of a less typical metal composition found in (a) bunker and (b) sludge oil. The sum of the concentrations of Ca, V, Fe, Ni and Zn has been normalized to 100%.

5. CONCLUSIONS

The difference observed in the metal content of fuel and waste oils provides an efficient way of identification. In the vast majority of comparisons, an identification is possible. In instances where illegal replacement of sludge by bunker oil has to be suspected, the metal composition would vary between that of the separate oils (with respect to the mixed volumes) thereby possibly obscuring the characteristic differences.

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