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DETERMINATION OF HEAVY METALS IN FUEL OILS AND AN ESTIMATION OF THE EMISSIONS OF HEAVY METALS FROM OIL COMBUSTION

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DETERMINATION OF HEAVY METALS IN FUEL OILS AND AND ESTIMATION OF THE EMISSIONS OF HEAVY METALS FROM OIL COMBUSTION

Abstract

In view of the extensive use of fuel oil in Sweden, even very low concentrations of pollutants in the flue gases formed during combustion would be expected to make substantial contributions to the total ambient air levels. This investigation was carried out to obtain an estimate of the level of the heavy metal emissions from fuel oil combustion. Different fuel oils were analysed as to their concentrations of As, Cd, Co, Cr, Cu, Fe, Hg, Mn, No, Ni, Pb, V and Zn. It was found that, when compared to other known emissions of heavy metals in Sweden, only the Vanadium and Nickel emissions (600 and 200 tons/year respectively) would contribute significantly to the total levels of immission.

Introduction

Fuel oil consumption in Sweden at present amounts to over 20 million m^3/year and is expected to increase further in the next few years. In view of this quite substantial consumption it can be assumed that the trace elements in the oil, which during combustion are emitted to the atmosphere with the flue gases, largely contribute to the total levels of immission.

From the air protection point of view, the chief interest has been focused on the soot and sulphur emissions from oil combustion. However, earlier investigations (1) have shown that certain heavy metals, above all vanadium, can be expected to cause considerable immissions (Table 1). The content of heavy metals in various oils shows great variations, and an idea of the average concentrations can be obtained only by analysis of a large number of oils.

The objective of this investigation has been to assess the importance of the emissions of heavy metals to the total levels of immission.

Emission of heavy metals should naturally be investigated in the outgoing flue gases, but a good estimation can be otbtained by analysing the oil. Without particle precipitators, nearly all the heavy metals present in the oil would be emitted to the atmosphere with the flue gases.

Earlier Investigations

Only very few investigations concerning trace metal concentrations in fuel oil have been made. US Department of Health, Education and Welfare (1) have published an inventory guide concerning emissions related to oil combustion. According to this guide, the composition of the ash from fuel oil varies widely, and a large number of elements have been detected. Normally, S, Al, Ca, Fe, Ni, Si, Na and V are present in the oil in complex organic compounds. Other elements, such as Ba, Cl, Cr, Cu, Au, Pb, Mo, Ag, Sr, Tl, Sn and Zn have been found at very low concentrations in the ash.

Table 1 shows the concentration of heavy metals in certain crude oils (2, 3).

In another investigation, concentrations of mercury in fuel oil and petrol were determined in 29 oils of varying origin (4). Low concentrations, with a maximum of 9,5 ng Hg/ g (n=29), were found.

Milner (5) reports results of analyses of ash from 24 crude oils with respect to their content of heavy metals.

Materials and Methods

A total of 37 oils (fuel oil qualities Eo 1-5, see table 2), collected during January 1972 from different oil companies in the Gothenburg area, were analysed. Eight of these oils were analysed by neutron activation. The distribution of oil qualities between oil companies is shown in Table 2.

The method of analysis was based on atomic absorption preceded by wet ashing of the samples according to Horeczy (6): The oil is mixed with sulphuric acid and heated until a dry cake remains. This cake is ashed in a muffle furnace (550° C). The remaining ash is dissolved in concentrated nitric acid and diluted with distilled water.

The analyses were carried out by means of a Pye Unicam SP 90 atomic absorption spectrophotometer. The concentrations of Co, Cr, Cu, Fe, Mn, Mo, Ni, Pb, V and Zn were determined. Also Ti, Cd and Hg were of interest, but the concentrations too low to be determined by atomic absorption. However, Cd, Hg and As were determined by neutron activation at the Isotoptekniska Laboratoriet, Stockholm*).

Since the sample preparation is relatively time-consuming, a simplified method was tried involving dilution of the oil to suitable viscosity with an organic solvent prior to atomic absorption analysis (7, 8). However, this method proved to be unsatisfactory, mainly because of instability of the flame during analysis. Moreover, the concentrations of many of the metals present were so low that they could not be detected by this method.

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The modified wet ashing procedure used has been compared by Horeczy with high temperature ashing (6). His results show that the most part of the substances forming porphyrine complexes (Fe, Cu, Ni and V) is lost at high temperature ashing, whereas with the modified wet ashing method, the losses are negligible.

In order to ascertain the reproducibility of the wet ashing method, certain oils were analysed twice. The results are presented in Tables 3-6. Moreover, known amounts of Fe, Mn, Ni, Pb and V and Zn were added to some of the oils; these samples were treated and analyzed in the same manner as the others. Results of the duplicate analyses show relatively good agreement, whereas in the samples containing added metal concentrations, deviations occur with respect to Ni and Fe. (Table 9)

Results

The results of the analyses are presented in Tables 3-6. They show that fuel oil Eo 1 contains very low concentrations of metals, compared to the heavier oils. Mostly the concentrations found are below or just around the detection limit of the method of analysis.

In the heavy oils (Eo 3-5) the concentrations of the metals studied are clearly above the detection limit (with the exception of Mo and, to some extent, Cr). Heavy metal content varies greatly between the oils. However, no such variation can be observed between the oil qualities Eo 3-5; here the metal concentrations seem to be independent of the quality. Oils with low sulphur content, on the other hand, usually contain lower metal concentrations than those with high sulphur content.

The heavy metals present at the highest concentrations are V, Ni and Fe: over 1 ppm in all of the oils Eo 3-5. The other metals examined appear in concentrations below or around 1 ppm.

Estimation of Emissions

The results of the oil analyses formed the basis for an estimate of the total emissions of heavy metals in Sweden from fuel oil combustion. Statistical data on the oil consumption in Sweden were provided by the Svenska Petroleum-institutet*) (Table 7). The calculations were based on the mean values of the heavy metal concentrations found in each oil quality (1-5) (Table 8). It was assumed that all the heavy metals in the oil are emitted into the atmosphere together with the flue gases.

Discussion

A comparison of these results with other known emissions of heavy metals in Sweden (table 10) shows that only vanadium and nickel emissions from oil combustion have any substantial influence on the total levels of immission. According to Rühling and Tyler's investigations (10, 11, 12) of a certain moss (*Hypnum cupressiforme*) from different built-up areas in Scandinavia, the contribution of vanadium from oil combustion is considerable; from their results it is clear that this is characteristic of an urban area independently of any industrial activity in that area.

To calculate fall-out of heavy metals on the basis of moss analyses is very precarious. However, Rühling and Tyler's results of such analyses show that the vanadium fall-out in Sweden is around 1 mg/m^2 per year, which makes a total fall-

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out over Sweden of about 400 tons a year. This figure is in good agreement with the total emission of vanadium estimated in this investigation.

For more comprehensive data on the most important (V and Ni) emissions from oil combustion, an extended investigation is required, involving a large number of fuel oils collected over a long period from different parts of the country. In addition, the concentration of other relevant elements in the oil samples should be investigated, such as Be, F, Cl and P.

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Table 1

The concentration (ppm) of heavy metals in certain crude oils

	V	Ni	Fe	Cu
Santa Maria, Calif.	223	97	17	0,3
East Texas	1,2	1,7	3,2	0,4
Louisiana	traces	5,65	0,70	...
Kuwait	22,5	6,6	0,33	0,02
Redwater, Canada	4,5	10,6	...	... (3)

	Venezuela Bachaquero	Venezuela Boscan	Venezuela San Joaquin
V	370	1400	0,6
Ni	46	100	0,2

	Irak Ain Zalah	Kuwait	Iran Gach Saran
V	95	30	114
Ni	15	6	... (2)

Table 2

Fuel oil qualities used in the investigation
(ls = low sulphur content)

Qualities:

	Eol + diesel	Eo3	Eo4	Eo5
Samples from::	Ara	BP	BP	BP
	BP	Esso	Gulf	Esso Bunker C
	Esso (2)	Gulf	Nynäs	Nynäs
	Gulf	Nynäs	OK	Shell
	Nynäs	OK	Shell	Esso Bunker C (ls)
	OK	Shell	Texaco	Nynäs (ls)
	Shell	Ara (ls)	Ara (ls)	
	Texaco	Nynäs (ls)	Nynäs (ls)	
	Ara diesel	Shell (ls)	Shell (ls)	
	BP diesel			
	BP mann diesel			

Eol = Domestic Fuel Oil
Diesel= Automotive (Gas Oils)
Eo3 = Fuel Oil 220"RI
Eo4 = Fuel Oil 650"RI
Eo5 = Fuel Oil 1500"RI
Bunker C = 3500"RI

Table 3

Heavy metal concentrations in Eol and diesel (12 samples).

Oil sample No.	V µg/g	Ni µg/g	Fe µg/g	Mn µg/g	Cu µg/g	Zn µg/g	Pb µg/g	Cr µg/g	Co µg/g	Mo µg/g	Cd ng/g	As ng/g	Hg ng/g
1	<0.08	<0.04	0.16	0.02	0.32	0.19	0.16	0.025	<0.02	<0.08			
2	<0.09	<0.04	0.22	<0.02	0.03	0.03	<0.2	0.02	<0.02	<0.09			
3	<0.09	<0.04	0.33	<0.02	0.07	0.01	0.08	<0.02	<0.02	<0.09			
4	<0.09	<0.04	0.17	<0.02	0.05	0.07	0.03	<0.02	<0.02	<0.09			
5	<0.09	0.03	0.57	<0.02	0.06	0.03	0.55	0.03	<0.02	<0.09	<10	1	4.1
6	<0.08	<0.04	0.20	<0.02	0.03	0.01	0.03	<0.02	<0.02	<0.08			
7	<0.09	<0.04	2.87	<0.02	0.08	–	0.05	<0.02	<0.02	<0.09	<10	41	2.7
8	0.08 <0.10	<0.03 0.10	0.14 0.14	0.02 0.06	0.25 0.09	0.47 0.09	0.03 <0.02	0.06 0.07	<0.02 <0.02	<0.08 <0.10			
9	<0.09	0.09	0.44	<0.02	0.06	0.06	0.05	0.05	0.02	<0.08			
10	<0.09	<0.04	0.25	<0.02	0.06	–	0.02	0.04	<0.02	<0.09			
11	<0.09	<0.04	3.30	0.02	0.18	0.07	0.10	<0.02	<0.02	<0.09			
12	<0.09	<0.04	0.43	<0.02	0.08	1.32	0.26	<0.02	0.03	<0.09			
Mean value	<0.10	<0.04	0.76	<0.02	0.10	0.09	0.11–0.13	0.02–0.03	<0.02	<0.10	<10	21	3.4

Table 3

Table 4

Heavy metal concentrations in Eo3 (9 samples)

Oil sample No.	V µg/g	Ni µg/g	Fe µg/g	Mn µg/g	Cu µg/g	Zn µg/g	Pb µg/g	Cr µg/g	Co µg/g	Mo µg/g	Cd ng/g	As ng/g	Hg ng/g
1	12.6	12.6	4.63	0.08	0.60	0.26	0.17	<0.02	0.57	<0.09	<10	100	1.8
2	31.6	12.3	2.02	0.05	0.12	1.10	0.39	0.04	0.32	<0.09			
3	3.91	8.15	11.2	0.15	0.08	0.11	0.07	0.03	0.58	<0.09			
4	111	17.3	4.08	0.03	0.15	0.19	0.79	0.02	0.18	0.23			
5	130	17.1	5.12	0.09	0.13	1.29	2.77	0.03	0.34	0.19	<10	41	2.7
6	143.8	21.9	2.62	0.10	0.37	4.43	1.01	0.07	0.20	0.25			
7	24.7	15.0	3.35	0.05	0.10	0.32	0.64	0.04	0.16	<0.09			
8	6.40	11.2	4.08	0.05	0.09	0.37	0.45	0.03	0.73	<0.09			
9	103	15.6	2.13	0.03	0.10	0.14	0.10	0.03	0.18	0.13			
Mean value	63.0	14.6	4.36	0.07	0.19	0.91	0.71	0.03	0.36	0.09–0.14	<10	70.5	2.25

Table 5

Heavy metal concentrations in Eo4 (9 samples)

Oil sample No.	V µg/g	Ni µg/g	Fe µg/g	Mn µg/g	Cu µg/g	Zn µg/g	Pb µg/g	Cr µg/g	Co µg/g	Mo µg/g	Cd ng/g	As ng/g	Hg ng/g
1	51.7	20.7	3,27	0.03	0.56	0.14	0.95	0.09	0.09	0.52			
2	10.9	13.0	6.08	0.10	0.35	0.95	0.85	0.05	0.62	0.09	≤30	12	2.7
3	66.8	10.8	7.49	0.10	0.18	0.66	1.34	0.03	0.28	0.17	≤10	114	2.2
4	83.3	25.0	9.59	0.08	1.23	1.24	1.17	0.05	0.11	0.13			
	83.8	26.4	9.68	0.08	0.88	1.22	0.88	0.04	0.12	0.35			
5	62.6	14.1	6.01	0.10	0.28	0.41	1.73	0.08	0.33	0.17			
6	32.3	20.9	6.64	0.15	0,17	1.00	1.33	0.04	0.23	<0.10			
7	8.4	10.7	4.00	0.07	0.11	0.34	0.77	0.05	0.80	<0.09			
8	14.6	21.2	1.38	0.07	0.26	0.30	0.07	0.02	0.83	0.26			
9	2.70	9.80	0.10	0.20	0.12	0.12	0.05	0.03	0.65	<0.09			
	2.74	10.5	13.2	0.20	0.13	0.15	0.04	0.05	0.69	<0.09			
Mean value	30.1	16.4	5.67	0.10	0.34	0.57	1.02	0.05	0.44	0.16–0.19	<30	63	2.5

Table 5

Table 6

Heavy metal concentrations in Eo 5 and Bunker C (6 samples)

Oil sample No.	V µg/g	Ni µg/g	Fe µg/g	Mn µg/g	Cu µg/g	Zn µg/g	Pb µg/g	Cr µg/g	Co µg/g	Mo µg/g	Cd ng/g	As ng/g	Hg ng/g
1	63.5	11.1	5.54	0.08	0.14	0.67	1.55	0.09	0.29	0.25			
2	10.7	5.93	2.87	0.03	0.29	0.49	0.17	<0.02	0.24	<0.10			
3	85.4	18.0	4.22	0.05	0.29	0.28	0.07	0.03	0.32	<0.07	<10	57	2.2
	84.3	16.8	4.85	0.05	0.34	0.28	0.07	0.02	0.37	0.13			
4	89.1	15.8	5.14	0.12	0.20	1.08	1.98	0.04	0.50	0.28			
	90.4	14.6	4.41	0.12	0.11	0.74	1.32	<0.02	0.44	0.28			
5	22.7	7.01	3.60	0.06	0.29	0.29	0.54	0.02	0.21	<0.08			
	27.8	6.62	3.86	0.07	0.27	0.37	0.49	0.03	0.19	<0.09			
6	42.3	23.1	7.68	0.08	0.15	1.09	1.44	0.06	0.19	<0.09	<10	23	2.6
Mean value	52.8	13.3	4.86	0.07	0.22	0.63	0.90	0.06	0.29	0.15-0.20	<10	40	2.4

Table 7

Fuel oil deliveries in Sweden
(in units per 1000 m^3)
1970 and 1971.

	1970	1971
Eo 1-2	8962	8526
Eo 3	2545	2233
Eo 4	5345	4326
Eo 5	7018	6448

Table 8

Estimated total emission of heavy metals in Sweden

tons/year

	Eo 1	Eo 3	Eo 4	Eo 5 & Bunker C	Total
1970					
V	<0.75	150	150	360	660
Ni	<0.30	34	82	89	200
Fe	5.8	10	28	33	77
Mn	<0.15	0.17	0.5	0.5	1.2
Cu	0.75	0.45	1.7	1.5	4.4
Zn	0.70	2.2	2.9	6.0	12
Pb	0.90	1.7	5.1	4.3	11
Cr	0.20	0.07	0 25	0.4	0.9
Co	<0.15	0.85	2.2	2	5
Mo	<0.75	0.27	0.90	1.2	2.6
Cd	<0.075	<0.025	<0.05	<0.07	<0.22
Hg	0.050	0.005	0.013	0.016	0.08
As	0.008	0.17	0.36	0.27	0.8
1971					
V	<0.7	130	120	330	580
Ni	<0.3	32	67	82	180
Fe	5.4	9	23	30	67
Mn	<0.15	0.15	0.4	0.43	1
Cu	0.7	0.4	1.4	1.4	3.9
Zn	0.65	1.9	2.3	5.5	10
Pb	0.85	1.5	4.1	3.9	10
Cr	0.18	0.06	0.21	0.37	0.82
Co	<0.15	0.75	1.8	1.8	4.4
Mo	<0.70	0.24	0.71	1.1	2.4
Cd	<0.07	<0.02	<0.04	<0.06	<0.2
Hg	0.05	0.005	0.01	0.015	0.075
As	0.007	0.15	0.29	0.25	0.70

Table 9

Results of analyses of fuel oils with known additions of heavy metals

µg

Element	Test 1	Test 2	Test 3
Vanadium			
Initial content	2.6	<3.0	<2.9
Initial content plus addition	213	210-213	210-213
Result of analysis	225	225	225
Nickel			
Initial content	<1.0	<1.3	2.9
Initial content plus addition	30.3-31.3	30.3-31.6	33.2
Result of analysis	20.0	25.0	22.5
Iron			
Initial content	4.6	7.3	14.2
Initial content plus addition	35.1	37.8	44.7
Result of analysis	40	62.5	35
Zinc			
Initial content	3.0	1.0	1.9
Initial content plus addition	22.1	20.1	21.0
Result of analysis	22.0	34.5	20.8

Table 9, cont'd.

	Test 1	Test 2	Test 3
Manganese			
Initial content	1.3	<0.7	<0.6
Initial content plus addition	18.9	17.6-18.3	17.6-18.2
Result of analysis	15.0	16.3	15.0
Lead			
Initial content	0.7	6.7	1.6
Initial content plus addition	17.2	23.2	18.1
Result of analysis	22.5	27.5	20.0

Table 10

Heavy metal emissions from oil combustion compared with other known emissions of heavy metals

1971

Element	Heavy metal emission from oil combustion ton	Other known emissions
Pb	10	Lead-resmelting industry: 500 t/year Car fumes: approx.1800 t/year
Cd	0.2	Copper resmelting industry:10-70 t/year
g	0.075	Chloralkali industry: 2.5 t/year Coal and coke: 130 t/year
V	580	
Ni	180	Iron works: 40 t/year
As	0.70	Coal combustion: 350 t/year
Cr	0.82	Iron works: 650-700 t/year
Mn	1	Iron works: 1000-2300 t/year
l	10	Iron works: 400 t/year
Cu	4	Copper resmelting industry : 775 t/year