

Trace and minor element characterization of diesel soot

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Summary. Concentrations of 20 trace and minor components, such as metals, nitrogen and sulphur, were determined in representative diesel soot samples corresponding to various driving patterns of an old and a new type of Mercedes-Benz diesel engine for passenger cars. The samples were analysed by instrumental neutron activation analysis, and after decomposition, by flame and graphite furnace atomic absorption spectrometry. The content of sulphur was determined by a method based on the formation of hydrogen sulphide and precipitation micro-titrimetry. The concentrations of the elements Au, La, Sb, Sc, and V were at the sub- $\mu\text{g/g}$ level; As, Ba, Cd, Co, Cr, Mn, Ni, and Se were at the lower $\mu\text{g/g}$ level; and Ca, Cu, Fe, N, Na, Pb, S, and Zn ranged from the upper $\mu\text{g/g}$ to lower percent levels. The emission of several elements was likely the result of different factors such as utilization of organometallic additives (Ca, Na, Zn) in diesel fuel or lubrication oil, contamination of diesel fuel by alkyllead compounds, wear and corrosion of the engine and exhaust system parts. The concentration of elemental components in diesel soot, generally, varied with operating conditions, which affected fuel and oil consumption, combustion efficiency (soot production), and mechanical strain.

Introduction

Diesel engines are one of many sources that contribute to air pollution. Diesel engine particulate emissions are about ten times higher than those by non-catalyst gasoline engines particulate emissions [1]. The particulate phase of diesel exhaust appears to be associated with hydrophobic components of urban and continental aerosols [2]. Numerous investigations have shown that soot emissions reach values up to 1 g/mile depending on the engine type and driving conditions [3]. At the present time, annual soot production by passenger cars and trucks in the FRG is approximately 55,000 t. In order to decrease toxic exhaust emissions, vehicles must meet particulate emission standards. For instance, the Environmental Protection Agency (EPA) particulate certification standard for light-duty diesel engine vehicles, effective since 1987, is 0.2 g/mile. However, 1990

Clean Air Act Amendments [§ 203 (g) (2)] prescribe particulate emission standards for light-duty vehicles and for light-duty trucks of 0.08 g/mile and 0.1 g/mile reaching full implementation in 1996 and 1997, respectively.

The composition of diesel exhaust is extremely complex and is influenced by engine type, speed and load, driving patterns, air-to-fuel ratio, operation temperature, fuel composition, and oil consumption. Polycyclic aromatic hydrocarbons (PAH) and nitroarenes (nitro-PAH) present in trace concentrations in the exhaust [1] are potential carcinogens and mutagens. Therefore, most investigations of soot composition have been especially oriented to organic components. The composition of the soot phase with respect to inorganic minor and trace components has been investigated much less. Concentrations of toxic and non-toxic metals in soot [3] have been reported over several orders of magnitude, from $\mu\text{g/g}$ to percent levels.

Various organometallic compounds such as metal naphthenates, dialkyldithiophosphates, and cyclopentadiene complexes are used as antioxidative or low wear additives for lubricating oils and as additives and catalysts for diesel fuel to optimize the combustion process (to decrease combustion temperature, increase combustion efficiency, suppress soot formation, and to improve soot oxidation [4–9]). A combination of convenient additives and ceramic particulate traps (filters) minimizes the emission [4, 10].

Environmental and health aspects of diesel soot emission require an improved knowledge of the composition of soot particulate matter. In addition, analytical characterization of soot for metallic components can be very useful in the investigation of the chemistry of burning and corrosion processes taking place in a diesel engine [11, 12], in the study of the role of chemical treatment of fuel, in the investigation of leachability and/or bioavailability for some toxic metals, etc.

In this work, representative diesel soot materials collected over various driving patterns with an old and a new type of Mercedes-Benz diesel engine for passenger cars were characterized for trace and minor inorganic components, especially metals.

Experimental

Diesel soot sampling

Representative diesel soot particulate matter was sampled from the exhaust of common naturally aspirated (non-turbocharged) 4-, and 5-cylinder OM 616 and OM 602 type

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Table 1. Sampling parameters for collection of soot on both engines tested

Old OM 616 engine	Operating conditions (turning speed, min ⁻¹ /power, Nm)				
	2000/10	2000/105	3000/105	4000/10	4000/51
Lambda ^a	5.77	1.84	1.65	3.74	2.26
Temp. of exhaust gas, °C	148	425	534	273	401
Consumption of diesel fuel, ml · min ⁻¹	37	111	185	109	181
Soot emission, mg · min ⁻¹	141	101	120	450	903
New OM 602 engine	Operating conditions (turning speed, min ⁻¹ /power, Nm) ^b				
	2000/14	2000/110	3000/120	4000/29	4000/78
Lambda ^a	5.58	1.83	1.69	3.64	2.29
Temp. of exhaust gas, °C	137	393	478	241	360
Consumption of diesel fuel, ml · min ⁻¹	38	114	192	124	193
Soot emission, mg · min ⁻¹	129	86	116	234	182

^a Oxygen vs. fuel stoichiometric combustion ratio

^b Corresponding values for the same working conditions as for OM 616 engine

Table 2. Instrumental parameters and temperature program for GFAAS

Parameter/step	Element								
	Cd	Cr	Cu	Fe	Mn	Ni	Pb	Se	V
Instrumental parameters									
Wavelength, nm	228.8	357.9	324.7	248.3	279.5	232.0	283.3	196.0	318.4
Spectral band width, nm	0.7	0.7	0.7	0.2	0.2	0.2	0.7	2.0	0.7
Source setting, mA, W resp.	EDL	HCL	HCL	HCL	HCL	HCL	EDL	EDL	HCL
Graphite tube ^a	ord	pyro	ord	ord	pyro	pyro	ord	ord	pyro
Modifier ^b , mg	0.2	no	no	no	no	no	0.2	0.2	0.2
Temperature program ^c									
Drying ^d	for all elements 130°C, ramp 10 s, hold 15 s								
Charring temp., °C	300	900	900	900	900	900	500	600	900
	for all elements ramp 20 s, hold 10 s								
Atomization ^e temp., °C	2300	2700	2500	2700	2700	2700	2300	2500	2700
Ramp/hold, s	1/5	1/5	1/5	1/5	1/4	1/5	1/4	1/4	0/4 ^f
Int. gas flow, ml/min Ar	50	50	150	300	50	200	100	20	0
Cleaning	for all elements 2700°C, 2 s, 300 ml/min Ar								
Cooling	for all elements 20°C, 5 s								

^a Graphite tube: ord = ordinary electrographite (Part. No. 070699), pyro = pyrolytically coated (Part No. 091504)

^b Mg(NO₃)₂ · 6H₂O Suprapur Merck, FRG

^c Internal gas flow 300 ml/min Ar except atomization step

^d Sampling volume 20 µl

^e Recorder & magnet and READ commands were ON 5 s and 1 s, respectively, before start of atomization step

^f Max. power heating

diesel engines at test benches of Daimler-Benz AG, Stuttgart-Untertürkheim. The test engines were operated at various conditions, ranging from 10 to 100 Nm torque measured on an eddy current brake at 2,000 to 4,000 rpm. Common BP diesel fuel and BP Strata and BP Vanellus lubricating oils were used in all experiments. The engine exhaust was diluted with filtered air and cooled using a dilution tunnel under conditions recommended by EPA [13]. The particulate matter was sampled iso-kinetically for 10–20 min by means of a sampling line equipped with an EM 100 flow controlled turbine (Ströhlein Instruments, Kaarst, FRG) and with a

Table 3. Instrumental parameters for flame AAS (three-slot burner, air-acetylene oxidizing flame)

Parameter	Element		
	Ca	Na	Zn
Wavelength, nm	422.7	589.0	213.9
Spectral band width, nm	1.4	1.4	0.7
Radiation source	HCL	HCL	HCL
Setting, mA	25	8	10

special holder (diameter 257 mm) for Sartorius cellulose acetate membrane filters (type 11302-257-D, 3 µm pore size). The collected mass, typically of 0.1–0.2 g was determined by differential weighing of the pre-conditioned filter. The soot concentration in exhaust was determined by the rec-

ommended procedure [13] using parameters recorded simultaneously at the test bench and dilution tunnel. The most important data on sampling soot particulate matter on which the analytical investigations were performed are summarized in Table 1. Samples corresponding to various driving conditions were separately removed from the filter base by using a plastic scraper and placed in plastic tubes. No loss of mass was observed during 2 weeks storage of samples over silicagel in a desiccator.

Table 4. Main nuclear data for the indicator radionuclides (IRN) used in INAA

Element	IRN	$t_{1/2}$	Main γ -line, keV (intensity, %)
As	⁷⁶ As	1.1 d	559.1(45)
Au	¹⁹⁸ Au	2.69 d	411.8(86)
Ba	¹³¹ Ba	11.8 d	496.3(44)
Ca	⁴⁷ Ca	4.54 d	1297.1(75)
Cd	¹¹⁵ Cd	2.23 d	336.0(46)
Co	⁶⁰ Co	1925 d	1173.2(100)
Cr	⁵¹ Cr	27.7 d	320.1(10)
Fe	⁵⁹ Fe	44.5 d	1099.3(57)
La	¹⁴⁰ La	1.68 d	1596.5(96)
Mn	⁵⁶ Mn	2.58 h	846.8(99)
Na	²⁴ Na	15.1 h	1368.5(100)
Ni	⁵⁸ Co	70.8 d	810.8(99)
Sb	¹²⁴ Sb	60.2 d	1691.0(47)
Sc	⁴⁶ Sc	83.9 d	889.3(100)
Se	⁷⁵ Se	119.8 d	264.7(59)
Zn	⁶⁵ Zn	244.1 d	1115.5(51)

Sulphur determination

The content of sulphur was determined after reduction of inorganic sulphuric compounds to H₂S with a mixture of HI/HCOOH/H₃PO₄/Sb₂O₃ and its separation in a special still apparatus followed by microtitration using a cadmium volumetric solution and dithizone as an indicator [14]. For selective determination of inorganic sulphur, 0.6–0.8 mg of the sample was treated directly. For the determination of total sulphur, 5 mg of the soot sample was decomposed after Schöniger in an oxygen atmosphere and aliquots of the absorption solution were analyzed as mentioned above.

Nitrogen determination

A CHN-O-Rapid analyzer (Heraeus, Hanau, FRG) was used for the determination of nitrogen in diesel soot. The analysis was performed with sample portions of 2–3 mg.

Table 5. Concentration of elements in diesel soot of an old OM 616 engine type^a

Element ^b		Concentrations µg/g at different operating conditions (turning speed, min ⁻¹ /power, Nm)					LD ^c
		2000/10	2000/105	3000/105	4000/10	4000/52	
Ca	f	155 ± 20	750 ± 50	1260 ± 300	330 ± 30	270 ± 40	2
	i	—	915 ± 90	1237 ± 33	337 ± 45	—	
Cd	g	0.80 ± 0.2	1.9 ± 0.1	1.7 ± 0.3	0.65 ± 0.08	0.34 ± 0.05	0.01
	i	1.04 ± 0.2	2.9 ± 0.3	2.0 ± 0.3	0.95 ± 0.16	—	
Cr	g	1.0 ± 0.2	22.2 ± 0.3	11.6 ± 2.1	2.4 ± 0.1	1.3 ± 0.4	0.2
	i	0.8 ± 0.1	18.9 ± 2.5	10.0 ± 1.5	2.6 ± 0.3	1.2 ± 0.1	
Cu	g	36 ± 2	123 ± 29	89 ± 7	47 ± 26	14 ± 1	0.12
	i	30 ± 6	1104 ± 146	344 ± 30	52 ± 5	29 ± 3	
Fe	g	32 ± 4	940 ± 10	390 ± 30	55 ± 9	22 ± 1	0.1
	i	0.56 ± 0.05	19.9 ± 0.4	10.0 ± 0.2	0.83 ± 0.10	0.52 ± 0.05	
Na	f	34 ± 10	375 ± 5	128 ± 5	98 ± 15	68 ± 5	4
Ni	g	3.1 ± 0.1	27.4 ± 0.4	19.4 ± 1.6	11.8 ± 0.8	7.7 ± 0.7	0.03
	i	3.3 ± 0.5	44.0 ± 4.4	21.7 ± 2.2	11.7 ± 1.3	8.3 ± 0.7	
Pb	g	31 ± 2	60 ± 3	64 ± 12	25 ± 2	15 ± 2	0.2
	i	0.4 ± 0.1	2.4 ± 0.1	2.5 ± 0.8	0.5 ± 0.1	0.6 ± 0.1	
Se	g	0.4 ± 0.02	2.8 ± 0.2	6.2 ± 0.3	0.5 ± 0.02	0.7 ± 0.03	0.1
	i	<0.2	1.2 ± 0.1	0.8 ± 0.1	~0.2	<0.2	
V	g	<0.2	1.2 ± 0.1	0.8 ± 0.1	~0.2	<0.2	0.2
Zn	f	280 ± 70	1080 ± 50	1630 ± 40	400 ± 60	320 ± 10	3
	i	211 ± 13	1057 ± 78	1640 ± 120	362 ± 26	334 ± 21	
S _{total}	%	0.61 ± 0.04	1.11 ± 0.04	1.82 ± 0.04	0.57 ± 0.04	0.54 ± 0.01	
S _{inorg}	%	0.38 ± 0.02	0.91 ± 0.01	1.56 ± 0.01	0.39 ± 0.03	0.24 ± 0.01	
N _i	%	<0.1	<0.1	~0.1	<0.1	0.18 ± 0.02	

^a Two parallel microwave decompositions using PMD oven, mean values ± standard deviation estimated after Dean-Dixon procedure for AAS determination and mean values of 3 parallel sulphur, nitrogen and INAA determinations ± standard deviation, respectively

^b Method: g = GF AAS, f = flame AAS, i = INAA

^c LD = detection limit (3 times s.d. of blank value of decomposition procedure or background equivalent concentration)

Table 6. Concentration of elements in diesel soot of a new OM 602 engine type^a

Element ^b		Concentrations $\mu\text{g/g}$ at different operating conditions (turning speed, min^{-1} /power, Nm) ^a					LD ^c
		2000/14	2000/110	3000/120	4000/29	4000/78	
Au	i		in all samples ~ 0.002				0.00003
La	i		in all samples 0.04 ± 0.01				0.0004
Sc	i		in all samples $0.001 - 0.01$				0.0001
As	i	0.46 ± 0.13	1.48 ± 0.19	2.39 ± 0.58	0.86 ± 0.08	1.53 ± 0.26	
Ba	i	3.55 ± 0.48	4.63 ± 1.84	8.10 ± 3.35	3.66 ± 0.87	6.29 ± 1.68	0.3
Ca	f	270 ± 10	1040 ± 20	910 ± 10	630 ± 10	1160 ± 20	2
	i	283 ± 35	1089 ± 210	1057 ± 228	465 ± 139	1317 ± 91	28
Cd	g	0.33 ± 0.01	0.58 ± 0.03	1.44 ± 0.03	0.44 ± 0.03	0.62 ± 0.03	0.005
	i	0.53 ± 0.14	1.00 ± 0.16	2.13 ± 1.05	0.93 ± 0.31	1.44 ± 0.48	0.05
Co	i	0.82 ± 0.12	1.29 ± 0.22	5.50 ± 1.26	2.39 ± 0.15	5.25 ± 0.76	0.0002
Cr	g	1.8 ± 0.1	3.6 ± 0.1	5.6 ± 0.1	2.7 ± 0.1	5.3 ± 0.1	0.2
	i	0.87 ± 0.14	4.14 ± 0.69	5.31 ± 1.23	2.24 ± 0.05	6.27 ± 1.22	0.1
Cu	g	66 ± 4	122 ± 5	179 ± 5	169 ± 3	93 ± 3	0.5
Fe	g	94 ± 6	230 ± 5	332 ± 3	141 ± 3	248 ± 2	0.6
	i	52.4 ± 8	225 ± 30	304 ± 77	107 ± 6	282 ± 35	0.6
Mn	g	1.5 ± 0.1	3.3 ± 0.1	3.9 ± 0.1	2.4 ± 0.1	4.8 ± 0.1	0.02
	i	1.54 ± 0.32	3.23 ± 0.23	3.89 ± 0.32	2.06 ± 0.09	4.05 ± 0.30	0.02
Na	f	510 ± 20	400 ± 10	290 ± 10	480 ± 10	470 ± 10	2
	i	471 ± 31	371 ± 14	240 ± 19	409 ± 10	411 ± 29	0.3
Ni	g	3.6 ± 0.3	31 ± 1	25 ± 1	13 ± 1	25 ± 1	0.15
	i	4.28 ± 0.60	30.7 ± 2.3	30.2 ± 5.3	12.0 ± 1.7	27.9 ± 4.7	0.2
Pb	g	91 ± 4	262 ± 9	292 ± 11	170 ± 8	243 ± 8	0.1
Sb	i	0.07 ± 0.01	0.09 ± 0.01	0.11 ± 0.05	0.08 ± 0.01	0.14 ± 0.02	0.0003
Se	g	< 0.2	5.2 ± 0.3	7.1 ± 0.3	2.1 ± 0.2	5.7 ± 0.3	0.2
	i	0.59 ± 0.07	5.54 ± 0.63	7.58 ± 1.52	1.92 ± 0.11	5.62 ± 0.75	0.03
V	g	0.11 ± 0.01	0.33 ± 0.04	0.31 ± 0.02	0.22 ± 0.02	0.51 ± 0.03	0.1
Zn	f	180 ± 10	1080 ± 20	1150 ± 20	550 ± 20	940 ± 20	3
	i	172 ± 28	1108 ± 157	1105 ± 247	482 ± 21	1037 ± 158	0.05
S_{total}	%	0.83 ± 0.02	2.60 ± 0.06	4.22 ± 0.01	1.21 ± 0.05	2.60 ± 0.04	
S_{inorg}	%	0.56 ± 0.02	2.44 ± 0.05	4.10 ± 0.01	1.18 ± 0.04	2.44 ± 0.07	
N_s	%	< 0.1	~ 0.1	—	0.19 ± 0.03	< 0.1	

^a One high pressure decomposition using a Berghof autoclave, mean values of 4 repeated AAS determinations \pm standard deviation and mean values of 3 parallel sulphur, nitrogen and INAA determinations \pm standard deviation, respectively

^b Method: g = GFAAS, f = flame AAS, i = INAA

^c LD = detection limit (3 times s.d. of blank value of decomposition procedure or background equivalent concentration)

Decomposition procedure

For the decomposition of the soot samples necessary for the analysis by atomic absorption spectrometry, two decomposition systems were used, a DAE II high pressure PTFE-lined autoclave system (Berghof, Tübingen, FRG), and a PMD microwave oven system (Hans Kürner, Rosenheim, FRG). Using the first one, sample portions of 100 mg were mineralized with a mixture containing 4 ml of conc. sub-boiled nitric acid and 0.1 ml of conc. hydrofluoric acid (Selectipur-grade, Merck, FRG) for 12 h at 200°C. The resulting solution was filled up with subboiled water to a volume of 10 ml. Using a microwave oven system, about 50 mg of the sample was treated with 2 ml of conc. subboiled nitric acid in quartz inserts. In preliminary experiments the sample was not dissolved applying maximum power for 10 min without simultaneous cooling. However, complete decomposition of the sample was easily achieved involving lower power (stage 4) for 20 min. The volume of the solution was adjusted to 5 ml.

Using the microwave oven system, the detection limits were decreased, due to lower contamination risk and lower fluctuation of blank for several elements such as Ni, Cu, and Fe.

Atomic absorption spectrometry

The trace elements Cd, Cr, Cu, Fe, Mn, Ni, Pb, Se, and V were determined in the sample solutions by using a Perkin-Elmer 5000 Zeeman atomic absorption spectrometer equipped with a HGA 500 graphite furnace and an AS 40 autosampler. A Perkin-Elmer 400 atomic absorption spectrometer was used for the determination of the minor elements Ca, Na, and Zn by the flame technique (acetylene-air). For the determination of all elements excluding Se and V, the sample solutions were diluted 10 times, and the standard addition method was used. The instrumental parameters used are summarized in Tables 2 and 3.

INAA

For the determination of the elements As, La, Mn, and Na via short- and medium-lived indicator radionuclides, sample portions of about 40–50 mg and standards were irradiated for 1 h at a thermal neutron flux of $1.3 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ in the FRM-1 reactor, Garching, and for the determination of the other 12 elements via long-lived indicator radionuclides, the samples and standards were irradiated for 4 days at a

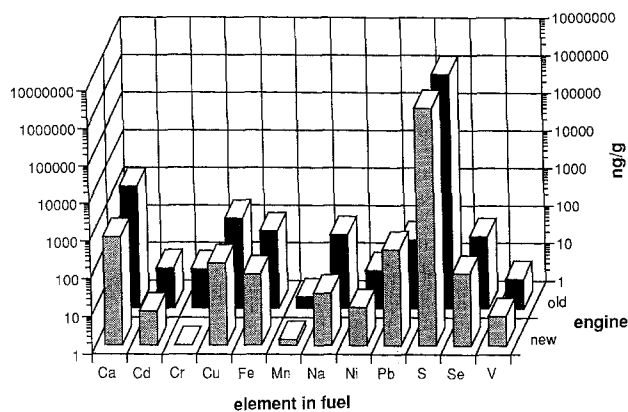


Fig. 1. Content of elements in diesel fuel used at the soot sampling

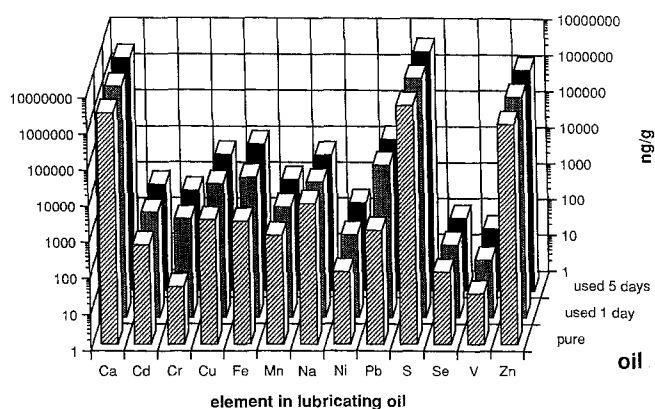


Fig. 2. Content of elements in lubricating oil used at the soot sampling

thermal neutron flux of $4 \times 10^{13} \text{ cm}^{-2} \text{ s}^{-1}$ in the FRG-2 reactor, GKSS Geesthacht, FRG. The most important nuclear data for the indicator radionuclides of the elements determined are given in Table 4. For the short irradiation mode, high-pressure polyethylene capsules (Stichting Hart Wool Research Foundation, Amsterdam, Holland) and for the long irradiation mode, Suprasil[®] quartz ampoules (Heraeus, Hanau, FRG) were used. Before use, they were cleaned with high-purity acids. Multielement standards were prepared in a clean bench by pipetting a suitable volume of the respective element stock solution into the ampoules and drying in a desiccator over Sicapent (Merck, Darmstadt, FRG) at reduced pressure and room temperature. After irradiation, the surface of the ampoules was cleaned by washing (polyethylene) or etching (Suprasil[®] quartz) before counting. Simultaneously, empty ampoules were proceeded in the same way in order to check the blank. For counting the irradiated samples and standards, we used a high resolution gamma-ray spectrometer system (EG & G Ortec, München, FRG) consisting of a Ge(Li)-detector (resolution 1.9 keV) and/or a NaI-detector $3'' \times 3''$, with an ADCAM multichannel buffer and with a DEC 350 professional computer. Evaluation was performed by software packages "Omnigam" and "Geligam" (EG & G Ortec, München, FRG).

Analysis of fuel and lubricating oil

In the determination of all elements except Pb and Se, aliquots of diesel fuel and lubricating oil samples, corresponding to patterns driven, were weighed and diluted in ratio 1:3 and 1:10, respectively, with analytical reagent grade xylene (Merck, Darmstadt, FRG) in cleaned polypropylene flasks. These solutions were analyzed by GFAAS and/or flame AAS applying conditions recommended in the Perkin-Elmer instruction manual and using the apparatus described above. Oil soluble standards (metal cyclohexane butyrates) supplied by Merck were used for standardization. For the determination of Pb and Se, 100 mg of sample were decomposed with 2 ml subboiled concentrated nitric acid in a quartz-lined autoclave of the PMD microwave oven system (Hans Kürner, Rosenheim, FRG) at power stage 4 for 20 min. The obtained sample solutions were analyzed by GFAAS under the conditions given in Table 2.

Results and discussion

The results obtained by all analytical methods used for soot from the old and the new engine are summarized in Tables 5 and 6, respectively. In most comparable cases, the results of the two methods agree within their experimental uncertainties. The results differ by more than 20% only in 10 of 97 comparable cases given in Tables 5 and 6. However, it should be noted that the uncertainties and discrepancies may result from both analytical errors and possible inhomogeneities regarding the distribution of elements in the soot. Occurrence of contamination errors was less probable, as is evident from the low values and their fluctuations observed in blank samples (see detection limits in Tables 5 and 6). Repeated analysis of soot samples was impossible because of the small amount of soot collected.

As is evident from Table 5 and 6, the minor and trace components investigated can be assigned to three groups by concentration levels: elements at sub- $\mu\text{g/g}$ level (Au, La, Sc, Sb, V); at lower $\mu\text{g/g}$ level (As, Ba, Cd, Co, Cr, Mn, Ni, Se); and at upper $\mu\text{g/g}$ to percent level (Ca, Cu, Fe, N, Na, Pb, S, and Zn). The relatively high concentrations of Ca and Zn are caused by the use of organometallic additives in lubrication oil. Although oil consumption is about 100 times lower than fuel consumption, Ca and Zn are present at concentrations about 1,000 times higher in oil than in fuel. The concentrations of elements in the fuel and lubrication oil are given in Figs. 1 and 2 in concise form. Wear and/or corrosion processes in engine and exhaust system may contribute to Cr, Fe, Mn and Ni emissions. Contamination of diesel fuel by alkyllead compounds from gasoline residues in transport equipments (see Fig. 1) may be the fluctuating source of Pb in diesel particulate matter. Differences in element content and in chemical form of sulphur in samples for various driving patterns of an engine tested (see Tables 5 and 6 for comparison) depend on combustion temperature, combustion efficiency, consumption of diesel fuel and lubricating oil, as well as on mechanical strain of engine parts. Thus, the different contents of elements and of inorganic sulphur relatively to the total sulphur for the old and new motor type may be explained by different combustion efficiency in the two motor types (see Table 1). The element concentrations are considerably influenced by soot production and/or by preconcentration processes in soot par-

titles during the combustion of a fuel. Soot emission of the new motor type was much lower when operating the engine at higher turning speed.

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