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유도결합 플라스마 원자 방출 분광법에 의한 LPG엔진에 사용된 윤활유 시료중의 마모금속 분석

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〈要　約〉

LPG엔진에 사용된 윤활유중의 마모금속 성분(Al, Fe, Cr, Si, Mg, Ca, P, Zn)등의 분석을 유도결합플라스마 원자 방출 분광법으로 실시하였다. 시료는 LPG를 사용하는 14대의 택시로부터 일정거리를 주행한 다음에 채취하여 분석하였다. 유도결합플라스마 원자 방출 분광기로 8종 원소의 동시분석에 필요한 최적 조작조건은 다음과 같았다. 1. 불꽃높이 : RF코일에서 16mm높이, 2. 시료분무 압력 : 125KPa, 3. 알곤기체유속 : 플라스마(냉각용) - 11.7L/min, 보조흐름 기체 - 1.7L/min, 시료 분무용 - 0.4L/min, 4. 라디오 주파 발진기 전력 : 1,400W, 5. 측정방법 : 10초씩 3회 측정한 값을 적분하였음. 한번 충전시킨 엔진 오일은 부족분만 보충하면서 계속적으로 사용하였으며, 10,000km주행시까지 계속 사용해도 Si이외의 마모금속 함량은 경고값에 미치지 않았으며 이 값들은 다음과 같았다. Al : 15.6 - 32.7ppm., Fe : 26.2 - 95.8ppm, Cr : 3.0 - 16.7ppm, Si : 11.9 - 33.0ppm(10.0 - 19.6ppm at 8,000km 차량번호 3903은 예외), Mg : 0.0038 - 0.043%, Ca : 0.055 - 0.185%, P : 0.075 - 0.10%, Zn : 0.100 - 0.132%. 일반적으로 이 값들은 낡은 차량에서 채취한 시료일수록 새것에서 채취한 것들보다 높은 경향을 보인다.

Determination of wear metals in worn lubricating oil in an LPG Engine by Inducively Coupled Plasma Atomic Emission Spectrometry(ICP AES)

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〈Abstract〉

Some analytical results of were metals(Al, Fe, Cr, Si, Mg, Ca, P and Zn) in an engine oil used by an LPG car were obtained by using Inductively coupled plasma atomic emission spectrometer. The samples were taken from 14 commercial LPG car at certain travelling distance;5,000km, 8,000km, 10,000km, 18,000 km and 20,000km. The optimum operating condition of the instrument for the simultaneous multi-elements determination was as follows : 1. Torch height : 16mm above the RFcoil, 2. Nebulization pressure : 125KPa, 3. Argon flow rate plasma(coolant) ; 11.7L/min, auxiliary ; 1.7L/min, nebulizer (carrier) ; 0.4L/min, 4. RF(radio frequency)power ; 1.400W(forward), and 1.0W(reflected), 5. Intergration time ; 10 sec x 3. The engine oil once charged in a LPG car could be used up to 10,000

km of travelling distance because the analytical result of the wear metals in the used lubricationg oil was below the value of warning limit(except Si) as follows : Al : 15.6 - 32.7ppm, Fe : 26.2 - 95.8ppm, Cr : 3.0 - 16.7ppm, Si : 11.9 - 33.0ppm(10.0 - 19.6ppm at 8,000km, except the car 3903), Mg : 0.038 - 0.043%, Ca : 0.055 - 0.185%, P : 0.075 - 0.10%, Zn : 0.100 - 0.132%. In general, the results showed higher values for old cars than those from new car.

Ⅰ. Introduction

Measurement of wear metals in worn lubricating oil has become an important means of monitoring the mechanical condition of engines, gearboxes and transmissions. An increase of somer metals in the oil is a good indication of abnormal wear of the components : The wear of cylinder or piston rings will show some increase of iron content in an engine oil. Aluminium is normally associated with pistons of bearings. Silica, however, may orginate from silicone anti - foam agents.

Contamination of metals such as calcium or zinc may be caused by dispersant or antiwear additives. Therefore, the accurate analysis of wear metals will provide some information on the condition of the oil itself as well as the engine. In fact, as the presence of certain metals is noticed or their concentrations begin to increase, the parts or components of the engine that are wearing out can be identified and replaced or repaired. Spectrophotometric methods have been used to determine the metal contents on a worn oil. These methods were time consuming and potentially inaccurate due to the process of ashing the oil and acid digestion. The spark analysis[1] is performed using a rotating graphite disk electrode. A spectrometer was employed to determine the spectra of ten or more elements in the 0.1 to 500ppm range 45 - sec exposure after 30 - sec spark. Direct examination methods such as atomic absorption[2,13,14] and atomic emission techniques were the most attractive methods until the introduction of ICP instrumention which is the most reliable and rapid method so far. The development of stable inductively coupled plasmas(ICP) by Reed in the early1960's[3,4] paved the way for the utilization in various applications. The application of ICP to atomic emission spectrocopy was separatively developed in two laboratories, Albright and Wilson in the U.K.[5,6,7] and the Ames Laboratiory, USAEC, in the U.S.A.[8,9]. The ICP instrument was commercialized in 1975 by the successive work[10] to explore their potential. Most of the applications to ICP involve the use of aqueous sample introduction with conventional nebulizers. The effects[11] of some organic solvents have also been studied and it was shown that solvents with a volatility comparable to or slightly highter than water require an increase in radio frequency(RF) forward power and additional plasma gas to produce a stable system. Some articles[12,15] on the determination of wear metals in used lubricating oils have also been reported by means of the ICP.

This work describes the direct determination method of some wear metals in used lubricating engine oil samples by using ICP - AES analytical system. The data obtained by the method could be applied for the decision of drain interval of the engine oil used.

Ⅱ. Experimental

The instrument used was a LABTAM model 8440 vacuum polychromator(Labtam Ltd., Victoria, Australia) together with a radio frequency(RF) generator(27.12MHz) and match box developed by the manufacturer. The performance of the nebruliser with respect to detection limits, precision, memory and acid effects analyse time has been carried out by multiprocessor Labtam 30 computer. The scanning monochromator 0.75m focal length vacuum instrument with a computer optimised Czerny - turner type optical system. The wavelength ranges of the monochromater were 3,000 - 8,000° A for the first order and 1,700 - 3, 000° A for the second spectra. The analytical lines are shown in Table 1. Standard solutions of each element were prepared from Conostan metalloorganic standards ; S - 21 blended standard or single-element standard(Conostan Division, Continental oil co., Ponca Oklahoma), by the dilution with the solvent, xylene. The standard lubricating oil samples ; 1084 & 1085, were obtaind from NBS, USA.

Table 1. Analytical Line of Elements

Element	Air	Vacuum	Spectrum	Slit (um)
Al	396.152	396.264	I	50
Ca	393.367	393.478	II	50
Cr	283.563	283.646	II	50
Fe	238.207	238.280	II	50
Mg	279.079	279.161	II	50
P	178.287	178.287	I	50
Si	251.611	251.687	I	50
Zn	213.856	213.924	I	50

A:I, neutral atom;II, singly charged ion

III. Result and Discussion

(a) Optimization of operating parameters.

Important parameters for optimisation are as follows ; (i)observation height in the plasma above the RF coil, (ii)Pressure of argon(carrier) gas in the nebuliser. (iii)flow rate of argon. A forward power of 1.4KW was used whilst determining optimum conditions. The net analytical measurements were determimed by subtracting the average of the blank from the sample values. The average value of three consecutive 30 second intergrations was taken as the experimental value throughout the work.

(i)viewing position in the plasma. Standard

Table 2. S/N ratio at various observation heights

Torch height mm / Element	10	11	12	13	14	15	16	17	18	19	20
Al	2.7	2.75	2.8	2.8	2.85	2.86	2.9	2.8	* 3.1	2.8	3.0
Ca	139.6	145.1	142.2	159.4	169.7	161.1	191.5	185.9	192.1	* 197.0	190.6
Cr	34.4	39.1	43.4	49.4	54.4	54.4	* 58.7	* 58.7	56.1	51.7	49.0
Fe	27.1	32.3	38.6	41.1	48.8	53.2	59.9	* 64.1	62.7	57.3	29.7
Mg	5	5	5	5	5	5	* 5	4	4	4	4
P	1.5	1.9	2.6	3.1	4.1	4.0	* 4.1	3.9	3.6	3.2	2.8
Si	10.6	11.5	12.6	12.5	14.3	14.8	* 15.5	15.4	14.9	13.9	13.7
Zn	43	53	56	59	71	73	* 83	82	* 83	74	72

* : the sign indicates optimum value.

solution(10 $\mu g/g$) of each element and blank(xylene) solutions were nebulized into the plasma to get the best signal to noise ratio(S/N) at various heights in the plasma over the RF induction coil. The variation of intensity(No of counts) to the viewing height was different from one to another. The signal to noise ratio(S/N) for the elements at a torch height is shown in Table 2. The most sensitive signal comes out for calcium. On the other hand, aluminium, magnesium and phosphous seem to be the least sensitive elements among the one tested. The optimum torch height for the simultaneous measurement of the eight elements could be compromised with 16mm above the RF coil.

(ii) Nelbulization pressure

The variation of nebulization pressure measured by dobbie pressure gauge(0 - 400KPa) gave great effect to the value of S/N ratio. The intensities designated by the number of counts were also variable to a different nebulization pressure. Table 3 shows the relationship between the pressure and the value of S/N. The pressure of 125KPa would be good enough for the simultaneouse determination of the elements except the one for calcium of 100KPa whose S/N ratio seems to be drastically decreased by increasing the pressure.

(iii) Argon fiow rate(L/min)

the spectrochemical analysis with the ICP discharge require more than one stream of argon gas. One argon stream(0.8 - 1.7L/min) carries the sample into the centre of the discharge to produce an effective pathway through the discharge. Second argon stream is confined to a volume near the tube walls to protect the quartz from the high temperatur(9,000 - 10,000K) discharge.

Pure solvent(xylene) and standard solution(10 ug/g) were aspirated into the plasma changing the gas flow rate at the argon pressure of 125 KPa. The relation between intensity (number of counts) for a single element and the gas flow rate is shown in Table 4. The optimum flow rate for the elements could be compromised with other values at 11.7L/min for the simulataneous multi - element analysis.

Table 3. S/N ratio at nebutisation pressure

Pressurekpa / Element	80	85	90	95	100	105	110	115	120	125	130	135	140	145	150
Al	1.7	2.0	2.2	2.4	2.6	3.0	3.3	3.6	4.0	4.2	4.5	4.6	* 4.6	4.3	4.1
Ca	91.3	94.3	104.9	135.3	* 135.7	90.1	81.3	30.1							
Ca	17.7	26.3	30.8	37.4	45.3	55.3	66.5	71.2	79.7	* 86.3	78.3	64.5	54.8	42.7	38.7
Fe	21.3	29.1	32.6	37.1	44.3	48.5	56.1	68.3	72.5	* 78.4	70.8	65.5	55.2	48.4	43.3
Mg	2.3	3.0	3.3	3.7	4.1	4.5	4.9	5.2	5.4	* 5.6	4.8	3.8	3.3	2.7	2.5
P	2.6	3.0	3.1	3.3	3.5	3.7	4.1	4.2	4.4	* 4.6	4.3	4.2	3.9	3.7	3.4
Si	5.3	6.7	7.5	8.8	10.2	12.1	13.6	14.2	17.5	18.0	* 18.3	16.8	15.3	13.3	12.9
Zn	37.2	48.5	53.0	60.4	69.8	75.0	86.6	90.5	113.7	* 115.6	112.3	111.4	96.1	86.2	84.6

*:the signs indicate the optimum values

(b) Preparation of calibration curves.

(i) a series of standard solutions of 0.1ppm, 1.00ppm, 10.0ppm, 100ppm and 500.0ppm for each element were prepared by the dilution with xylene solvent using the standard material, Conostan S - 21 which contains Ag, Al, B, Ba, Ca, Cd, Cr, Cu, Fe, Mg, Mn, Mo, Na, Ni, P, Pb, Si, Sn, Ti, and Z.

(ii) The calibration graphs of the eight elements were linear from 0.1ppm to 500.0ppm. The operating condition of the ICP is shown in Table 5. The condition was applied for the determination of the standard samples, NBS 1084 and 1085. The samples were diluted with xylene solvent whenever lower concentrations of the elements required. The results for the determination of the standard sample are shown on Table 6. The confidence ranges were calculated from the ten determinations for each element. The experimental values seem to be reasonably good agreement with the certified values, but some exception for Pb, Mg. The experimental condition on Table 5 was employed for all determinations throughout the work.

Table 4. S/N ratio at an argon flow rate

Flow rate, l/min / Element	10.6	11.0	11.3	11.7	12.3	12.6	12.8	1.32	13.8	14.2
Al	2.06	2.52	2.61	* 2.70	2.66	2.53	2.48	2.52	2.48	2.42
Ca	442	449	462	* 468	457	422	420	433	4.05	397
Cr	43.9	45.2	47.1	* 49.1	46.6	41.4	39.2	39.3	38.1	37.4
Fe	38.7	40.9	43.1	* 44.9	44.5	41.6	40.2	40.3	39.4	39.4
Mg	4.0	4.1	4.2	* 4.3	* 4.3	3.9	3.9	3.9	3.8	3.7
P	3.0	3.1	3.1	* 3.2	* 3.2	2.9	2.9	2.8	2.7	2.7
Si	10.1	10.4	10.7	* 11.2	10.6	9.8	9.3	9.2	9.0	8.8
Zn	73.2	73.6	75.5	* 77.6	74.5	66.5	67.2	66.7	63.3	62.3

* : indicates the optimum value

(c) Sample preparation and determination of the elements.

Three kinds of engine oils, E10W/30(SE/CC), S10W/30(SE/CC), U10W/40(SF/CC), produced by a Korean oil company were selected to be tested the elements in the oil used by several LPG commercial cars. The samples were made ten times dilution with xylene and agitation prior to weighing. Then 1.00gr sample was weighted into a clean weighing bottle. The dilution of oil samples with a solvent would be enevitable to minimise the variation of viscosity from one sample to another and also to maintain stable plasma condition.

Previous workers[11,12,13,17] prefer to use the solvents, methyl isobutyl ketone(MIBK) or xylene to dilute the oil samples.

At the begining, the cars were filled up with one of the engine oils, and then start to sample the oil at certain points of driving, such as 5,000, 8,000, 10,000, 15,000 and 18,000 and 20,000Km, respectively. The same kind of oil was added to the chamber of the car from time to time maintain the optimum level. The oil samples taken from the car were carefully diluted to 10 times with xylene. The samples diluted were used for the determination of the elements at the condition of ICP mentioned on Table 5.

The analytical results are shown in Table 7 for Fe, Cr, Si, and Al, and Fig. 1-4 for Mg, Ca, P and Zn.

Generally the wear metal contents in the oil gradually increased as the travelling distance is increased. On the other hand, the amount of additives such as Mg, Ca, P and Zn decreased as the mileage increased.

The result says that the lubricating oil once filled up in the chamber can be used up to 10,000Km for U10W/40(SF/CC) oil and 8,000Km for SE/CC grade (E10W/30 and S10W/30) by successive filling the oil to an optimum level. The Si content for the car 3903 was initially higher than the warning limit[18] (see Table 8) possibly due to poor air filtration, air leaks or contamination of product. In other words the wear metal contents in the used oil would not give any serious damage to the engine.

Table 5. ICP operating conditions

Argon flow rate	plasma(coolant)	11.7L/min
	Auxiliary	1.7L/min
	Nebulizer(carrier)	0.4L/min
RF power	Forward 1,400W	
	Reflected 1.0W	

Table 6. Analytical Results of NBS Materials

Sample / Element	conc./ppm					
	1084			1085		
	true value	exp. value	R.E(%)	true value	exp. value	R.E(%)
Al	98±2	97±2	−1.02	296±4	289±3	−2.36
Cr	100±3	103±2	+3.00	298±5	300±2	+0.67
Cu	98±4	92±3	−6.12	295±10	295±3	0
Fe	100±3	100±2	0	300±4	304±4	+1.33
Mo	97±5	97±2	0	292±11	290±3	−0.68
Ni	101±4	98±2	−2.97	303±7	310±4	−2.3
Pb	101±4	93±1	−7.92	305±8	284±5	−6.9
Mg	98±4	95±2	−3.06	297±3	280±5	−5.72
Ag	102	93±2	−8.82	296	295±3	−0.34
Ti	99±5	99±2	0	300±4	304±3	+1.33
Si		101±2	—	308	314±3	+1.95

The most important interelement interferences was the spectral interference. It was investigated by analysing wavelength-intensity profiles with a standard solution of each element(100$\mu g/g$). The profiles were produced by manually scanning the entrance slit along the Rowland circle using the profiling micrometer. No interference was found on the scanning monochromator at the analysing wavelength which was selected within 0.4 Å of the nominal line in the presence of interfering elements.

The slight increase in the spectral intensity could be observed for some elements due to the matrix effect.

Table 7. Analytical results of wear matals in an Engine oil

Elements(ppm) \ Car No		3930	3931	3932	3933	3934	3900	3901	3902	3907	3909	3903	3904	3905	3908
measured at a travel distance, Km		U10W/40(SF/CC					E10W/30(SE/CC)					S10W/30(SE/CC)			
	5,000	44.4	22.3	32.5	26.4	24.3	39.6	41.0	30.7	23.5	18.8	57.6	38.0	40.2	86.0
Fe	8,000	47.6	33.0	32.7	28.5	32.2	47.5	50.9	35.8	38.0	23.8	63.8	50.0	44.9	86.6
(<1)	10,000	82.8	51.7	29.0	26.2	37.4	54.7	61.4	39.0	81.3	44.9	87.4	89.0	61.5	95.8
(<1)	15,000	102	100.5	63.7	56.1	60.7	72.8	90.4	80	106.7	82.0	13.6	200.0	100	100.0
	18,000	109	109.4	73	65.5	61.4	79.7	113	98	133.4	82.9	149.1	230.0	115.3	10.0
	20,000	110	110.4	83.2	85.0	82.0	104.9	118.4	113	160.2	104.7	186	280	118.1	140.0
	5,000	3.9	3.5	4.2	2.7	4.0	6.3	7.0	4.8	3.4	2.5	4.3	3.3	3.5	5.3
Cr	8,000	4.3	4.0	4.4	2.5	4.2	7.8	9.3	6.5	5.6	3.5	6.1	4.2	3.9	6.3
(<1)	10,000	7.5	5.9	4.7	3.0	5.0	9.3	12.8	9.3	16.7	3.6	6.4	6.3	10.5	7.3
	15,000	8.7	9.5	9.4	6.0	8.0	10.3	16.9	18.3	20.9	6.7	12.1	13.1	14.1	9.5
	18,000	10.6	9.9	10.5	6.2	8.2	10.3	20.7	23.3	26.7	7.8	13.5	14.2	16.3	12.5
	20,000	11.8	10.1	10.9	9.5	13.0	16.2	22.2	283	28.7	10.1	13.7	14.9	16.8	13.0
	5,000	9.8	11.0	11.9	11.0	9.5	18.4	12.9	11.2	11.0	11.9	25.0	13.5	12.8	18.7
Si	8,000	14.2	11.3	11.6	11.2	10.0	19.6	14.5	13.2	12.0	11.1	29.2	17.3	13.2	18.0
(3-7)	10,000	16.0	17.2	12.3	11.9	12.9	20.3	20.0	14.0	29.9	12.0	31.2	33.0	32.8	15.3
	15,000	19.7	26.9	22.4	21.3	17.9	25.2	28.5	26.6	30.6	17.5	41.6	36.0	52.8	31.2
	18,000	20.4	28.6	24.7	26.2	20.3	27.9	30.4	28.6	31.1	20.6	45.9	43.8	65.2	30.4
	20,000	21.7	31.9	27.1	28.6	22.0	34.2	33.0	30.7	36.1	27.7	49.2	49.3	67.2	26.8
	5,000	11.0	12.6	12.3	8.5	3.0	11.6	11.8	11.0	15.7	13.3	26.7	26.2	20.2	31.7
Al	8,000	23.5	13.9	19.8	19.8	13.7	14.0	16.6	13.8	17.0	13.8	28.4	32.2	22.7	31.5
(<1)	10,000	26.8	20.7	20.6	22.3	18.3	18.1	18.8	16.8	17.3	15.6	29.0	32.7	27.4	21.8
	15,000	32.6	21.8	21.2	25.1	19.4	21.0	19.4	21.4	17.5	18.8	30.7	33.4	32.1	49.5
	18,000	32.7	22.0	23.0	25.9	21.7	26.2	22.4	21.8	18.3	20.2	35.5	40.0	33.8	31.4
	20,000	36.1	33.4	23.2	30.1	30.7	28.6	23.4	23.2	25.3	22.8	38.9	50.5	42.0	33.1
Deposit		clean	clean	clean	slight sludge	clean	clean	clean	slight sludge	clean	sludge	clean	sludge	sludge	sludge

*( ) values indicate those one in a new oil

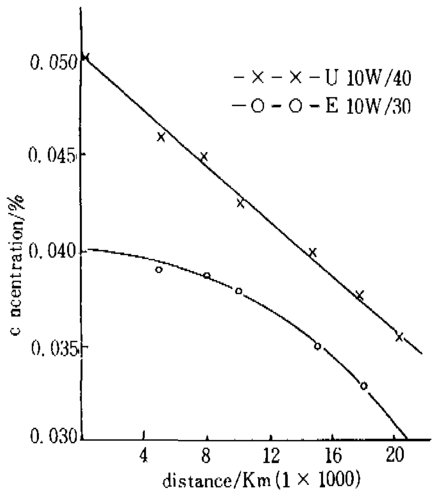

Fig. 1 Relation between the travel distance and Mg concentration (average) in used oil

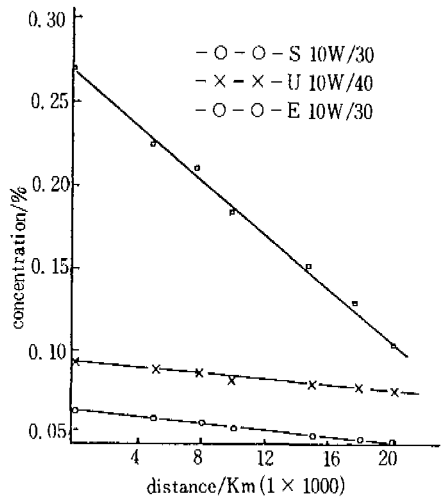

Fig. 2 Relation between the travel distance and Ca concentration (average) in used oil

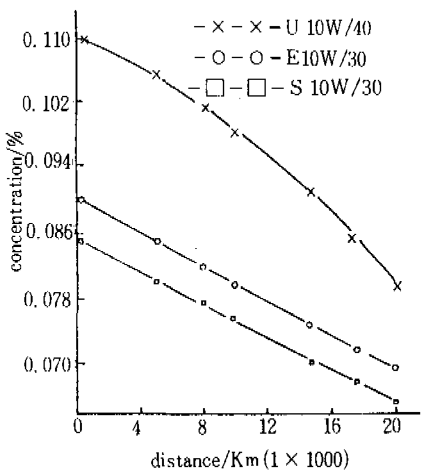

Fig. 3 Relation between the distance and P concentration (average) in used oil

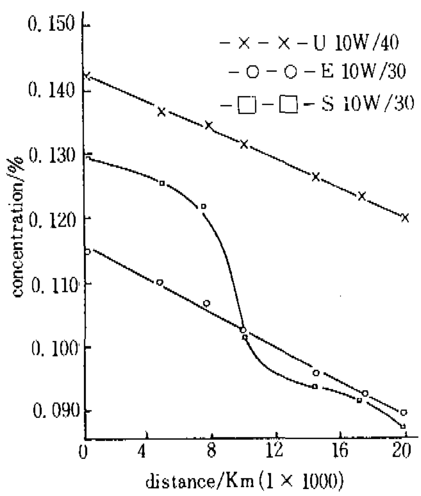

Fig. 4 Relation between the distance and Zn concentration (average) in used oil

A spectral intensity from very low level of nickel(1ppm) was severely depressed in the presence of magnesium based detergent additives by the effect. Al, Cr, Fe, Mg, P, Si and Zn could be satisfactorily determined in the range of one to 100ppm without any serious matrix effects. Silicon frequently showed up the effect at range of 3 to 6ppm level when the silicone deformants used.

Table 8. Recommended Warning Limits for Engine oil in service[18)]

Trace metals, ppm \ Engine	Gasoline Engines	Automotive Diesel Engines	Gas Engines
Aluminium	40	40	40
Boron	—	20	—
Chromium	40	40	40
Copper	40	40	40
Iron	100	100	100
Lead	40	100	40
Silicon	20	20	
Sodium	—	50	—
Tin	40	40	—

IV. Conclusion

ICP-AES (Inductively Coupled Plasma-Atomic Emission Spectrometry) was successfully applied for the routine analysis of some wear metals in an used lubricating oil. The oil was made dilution with the solvent, xylene to do direct analysis of some elements.

The optimum parameters for the simultaneous multielement analysis with the instrument were as follows :

a. Torch height : 16mm above the RF coil.
b. Nebulization pressure (carrier) : 11.7L/min
c. Argon flow rate - plasma (coolant) : 125KPa
auxiliary : 1.7L/min
nebulizer (carrier) : 0.4L/min
d. RF power forward : 1,400W
reflected : 1.0W
e. Intergration time : 10 sec x 3

The analytical results of the elements in an used lubricating oil at the traveling distance of 10,000Km were within the warning limit[18)] and are as follows:

Al;15.6-32.7ppm, Fe;26.2-95.8ppm, Cr;3.0-16.7ppm, Si;11.9-33.ppm(10.0-19.6ppm at 8,000Km, except for the car 3903), Mg ; 0.038-0.043%, Ca ; 0.055-0.185%, P ; 0.075-0.10%, Zn : 0.100-0.132%

The values of metal contents were generally shown higher walue for old car than the one for new car.

Therefore, the engine oil, SF/CC could use up to 10,000Km without drain , but 8,000Km for the engine oil, SF/CC grade in an LPG car.

Relative errors for the elements, Al, Cr, Fe, Mg and Si were -2.4, +3.0, +1.3, -5.7 and +2.0% respectively.

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