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The role of reference crude oils used in the determination of oil amount in sediments by UVF

Sedimentte petrol kirliliğinin UVF'de tayininde kullanılan referans ham petrolün rolü

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Abstract

In this work the influence of oil amount in sediment was determined using various reference oils by UVF. 15 reference oils which were transported from the Black Sea used for plotting of standard curve. The differences of oil amount found through reference oil equations were varied in sediment as 17.0-28.1 % in wet weight, 13.4-14.1 % in oven, 12.2-26.2 in freeze dryer. These results showed that reference oils have an important role on the amount of oil in sediment.

In the determination of oil pollution, the pollutant oil must be used in the analysis as references for each time.

Keywords: Sediment, reference oil, UVF.

Introduction

Oil pollution in sea water, sediment and marine organisms were determined using ultraviolet fluoro spectrometer (UVF), gas chromatography (GC), gas/mass spectrometer (GC/MS) and liquid

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chromatography (LC). GC/MS and LC method were especially used for the determination of oil components but not of all were dedected.

Oil contamination was generally measured by UVF using reference material as crude oil or chrysene. UVF technique depends on all fluorescence compounds exist in crude oil. They content various hydrocarbon compounds especially polyaromatic compounds which have fluorescence. The composition of crude oil was not the same. Erhardt and Petrick (1989) suggested that the usual reference substances is a crude oil likely to be used or transported in the area under investigation. In oil pollution literatures must state the reference oil used.

The crude oil composition change in each load. Therefore the oil amounts in the samples were not found similar due to polyaromatic compounds content of crude oil

The oil determination through chrysene reference is also have many problems while the amount of chrysene in oil are not similar. The chrysene reference was not exactly demonstrated the oil pollution in sea or sediment. For example chrysene amount in Kuvait and South Luisiana crude oils are 9 and 23 ppm, (Roy, 1997) respectively. The oil concentration value through reference chrysene was found in Rompe oil 5.4 and 59 ng/g in sediment (Villeneuve et al., 2007). Thus the results change in all experiments and the level found very lower than through crude oil refences.

UVF more frequently used technique for oil determination in seawater, sediment and marine organisms. This technique is sample and fast.

In this paper various reference crude oil were used for the determination of oil amount in sediments and difference on the results were discussed.

Material and Metod

The sediment samples were taken from Zonguldak, Turkey in the Black Sea at 2005 using Van Veen Grab. The oil amount of sediment was determined using various crude oils. Standard curve of crude oil solution were prepared in a concentration of 0.32 – 1.228 µg/ml in hexane. Its calibration curve and equation were taken from apparatus. UVF analysis was carried out using a Schimadzu ultraviolet fluorospectrometer 1601. The intensity was measured fluorescence at 310-360 nm (ex/em).

The reference crude oils were provided from TUPRAS refinery, İzmit, Turkey.

The reference oil and its concentration for plotting of calibration curve were;

1. REB oil (26.02.2005). 0.32-1.28 µg/mL
2. REB oil (08.06.2005). 0.32-1.28 µg/mL
3. REB oil (20.06.2005). 0.5-1.5 µg/mL
4. SEB (Rusya) (17.04.2005). 0.4-1.2 µg/mL
5. Siberian light (24.04.2005). 0.47-1.18 µg/mL
6. Siberian light (18.06.2005). 0.36-1.44 µg/mL
7. Rusya (2003). 0.25-1.5 µg/mL

These standard curves were used for measuring of oil content through different lot of oil.

The other reference oil used for the indicate of variation of equation.

1- Russian crude oil super 1995
2- Russian crude oil 1998. Number 1, 2, 3, 4
3- REB HP 2003
4- SEB 16.07.2006
5- SEB 31.08.2006
6- SEB 05.09.2006
7- SEB 16.10.2006
8- REB 23.11.2006

The calibration curve of these crude oil (nuber 1-8) was plotted in a concentration of 0.32-1.22 µg/ml.

Results

The standard equation of calibration curve for the tested crude oil are:

R1: $F_1 = 509.37 \times C + 5306$. $R^2 = 0.998$ (REB oil 26.02.2005)

R2: $F_1 = 425.40 \times C + 98.64$. $R^2 = 0.999$ (REB oil 08.06.2005)

R3: $F_1 = 428.96 \times C + 104.28$. $R^2 = 0.999$ (REB oil 26.06.2005)

R4: $F_1 = 534.51 \times C + 79.18$. $R^2 = 0.997$ (SEB oil 17.04.2005)

R5: $F_1 = 539.24 \times C + 51.83$. $R^2 = 0.992$ (Siberian light 24.04.2005)

R6: $F_1 = 500.48 \times C + 65.54$. $R^2 = 0.998$ (Siberian light 18.06.2005)

R7: $F_1 = 552.67 \times C + 5.55$. $R^2 = 0.987$ (Russian oil unknown, 2003)

The equation of calibration curve for the other reference oil used

1- $F_1 = 266.10 \times C + 64.49$. $R^2 = 0.999$ (Russian crude super 1995)

2- $F_1 = 279.01 \times C + 14.49$. $R^2 = 1$ (Russian crude oil no:1 1998)

3- $F_1 = 301.25 \times C + 32.64$. $R^2 = 0.999$ (Russian crude oil no: 2 1998)

4- $F_1 = 290.37 \times C + 16.91$. $R^2 =$ (Russian crude oil no:3 1998)

5- $F_1 = 328.14 \times C + 57.41$. $R^2 =$ (Russian crude oil no:4 1998)

6- $F_1 = 237.72 \times C + 92.23$. $R^2 = 0.997$ (REB HP 06.04.2003)

7- $F_1 = 829.78 \times C + 16.86$. $R^2 = 0.99$ (SEB 11.07.2006)

8- $F_1 = 874.9 \times C - 11.55$. $R^2 = 0.999$ (SEB 05.09.2006)

9- $F_1 = 875.08 \times C + 7.46$. $R^2 = 0.999$ (SEB 31.08.2006)

10- $F_1 = 817.46 \times C + 14.83$. $R^2 = 1$ (SEB 16.10.2006)

11- $F_1 = 816.37 \times C - 19.07$. $R^2 = 0.995$ (REB 23.11.2006)

Tables 1 and 2 show the results of oil amount in TRK13 and TRK14 calculated from the equation R1-R7.

Table 1. Oil amount calculated from wet weight sediment (mg/g)

Sediment sample	Reference crude oil	Station and sampling date	
		TRK 13 02.10.2005	**TRK 14 02.10.2005**
Wet weight	R1	0.985	1.099
	R2	1.073	1.209
	R3	1.051	1.186
	R4	0.890	0.999
	R5	0.933	1.041
	R6	0.978	1.094
	R7	0.911	1.016
Oven	R1	8.863	10.216
	R2	8.490	10.100
	R3	8.160	9.755
	R4	7.478	8.763
	R5	8.417	9.695
	R6	8.526	9.901
	R7	8.304	9.517
Freze dried	R1	10.365	18.057
	R2	8.229	17.357
	R3	7.648	16.690
	R4	7.970	15.262
	R5	9.879	17.147
	R6	9.576	17.386
	R7	9.900	16.835

Table 2. Oil amount calculated from dry weight sediment (mg/g)

Sediment sample	Reference crude oil	Station	
		TRK 13 02.10.2005	TRK 14 02.10.2005
The amount of oil was calculated after extraction of the sediment and the residue weight	R1	1.146	1.588
	R2	1.247	1.747
	R3	1.222	1.713
	R4	1.035	1.443
	R5	1.085	1.503
	R6	1.137	1.580
	R7	1.059	1.467
Oven	R1	11.856	14.260
	R2	11.358	14.098
	R3	10.916	13.616
	R4	10.004	12.231
	R5	11.260	13.533
	R6	11.406	13.821
	R7	10.999	13.218
Freze dried	R1	14.165	25.381
	R2	11.247	24.397
	R3	10.452	23.459
	R4	10.892	21.453
	R5	13.502	24.102
	R6	13.087	24.438
	R7	13.201	23.545

Tables 1-2 show the enfluence of reference oils equatşons on tha results. İt can be seen in this table the amount of oil in sediment was varied depending of each reference oil.

Tables 3-5 show minimum and maximum, differences percentage in oil level.

Table 3. Oil level differences in wet weight sediment

	Found	Difference	%
TRK 13	0.890 - 1.073	0.183	17.0

TRK 14	0.999 - 1.209	0.210	28.1

Table 4. Oil level differences in sediment dried using oven

	Found	Difference	%
TRK 13	7.478 – 8.526	1.048	13.4
TRK 14	8.763 – 10.216	1.443	14.1

Table 5. Oil level differences in sediment using freeze dryer.

	Found	Difference	%
TRK 13	7.648 – 10.365	27.17	26.2
TRK 14	15.262 – 17.386	2.12	12.2

Table 3-5 show the differences between the oil level found as 12.2-28.1 %.

Tables 6-7 show the differences of oven/wet weight, freeze dried/wet weight, freeze dried/oven in TRK13 and TRK14 sediment.

Table 6. Differences of oven/wet weight, freeze dried/wet weight, freeze dried/oven in TRK13)%).

Reference	Oven/Wet weight	Freeze dried/Wet weight	Freeze dried/Oven
R1	8.88	9.38	1.50
R2	7.42	7.16	- 0.26
R3	7.11	6.60	0.51
R4	6.48	7.08	0.49
R5	7.52	8.93	1.46
R6	7.54	8.59	1.05
R7	7.39	8.88	0.59

Table 7. Differences of oven/wet weight, freeze dried/wet weight, freeze dried/oven in TRK 14 (%)

Reference	Oven/Wet weight	Freeze dried/Wet weight	Freeze dried/Oven
R1	8.12	16.94	7.48
R2	8.89	16.14	7.23
R3	9.91	15.50	7.92
R4	7.76	14.26	5.56
R5	8.54	16.05	8.44
R6	8.80	16.29	7.47
R7	8.80	17.81	7.66

Tables 6-7 show the differences between the mothods used. The variation was 49-16.94 %.

When compared our finfings with Readman et al. (2002) made in the Black Sea sediment at 1995 including near of Bosphorus was 30-340 µg/g. These authors used Rompe oil equalent which is not transported through the Black Sea. We take also the sediment samples in the same area in 1995 and found oil pollution as 1.62-26.68 …… through Russian oil references..

As can be seen in this table the results are not the same, the oil pollution amount in sediment were varied the equation of reference oil and applied method for extraction. The equation of refernce oil number 1-11 show also the equation were changed depeding on load.

The results showed that reference oil has an important role in the determination of oil amount in sediment. There are not in literature on the this subject. In conlusion in oil pollution determination was made using the oil transported in the area investigated.

Özet

Bu çalışmada sedimentte UVF'de petrol kirliliği tayini için kullanılan referans ham petrolün rolü incelendi. Bunun için 2003-2006 yıllarında Türkiye'ye ithal edilen Karadeniz'den tankerle geçen ham petrol kullanıldı. UVF'de bunlara ait standart eğrileri çizildi ve denklemleri hesaplandı. Bu denklemler kullanılarak sedimentte petrol kirliliği tayininde farklı sonuçlar alındı. Bunun sonunda petrol kirliliği tayininde kullanılan referans petrolün rolünün çok büyük olduğu saptandı. Bu sebepten tayinleri devamlı olarak o bölgeden geçen ham petrolün referans olarak kullanılması gerektiği saptandı. Bugüne kadar yapılan tayinlerde petrol kirliliği tayininde krizen veya ham petrol

kullanılmaktadır. Ham petrolün içerisindeki krizen miktarının farklı olması sonucunda sonuçlar düşük çıkmaktadır. Ham petrol kullanılması halinde ise hata miktarı kullanılan referans ham petrole göre ve sedimentin kurutma tekniğine göre değiştiği saptanmıştır. Bu farklılık yaş sedimentte %28, etüvde kurutmada %14 ve liyofilizasyon tekniğinde %26'ya kadar değişmektedir.

Bu çalışma göstermiştir ki petrol kirliliğinin hesaplanması için devamlı olarak o bölgeden geçen ham petrole ait referans eğri kullanılmalıdır. Karadeniz'den geçen tankerlere yüklenen ham petrol Rusya, Azerbaycan, Kazakistan vd. ülkelerden menşeylendiği düşünülürse bu petrollerdeki yapısal faklılık dolayısıyla bir standarda göre yapılan petrol kirliliği tayininin sonuçları tartışma götürür.

References

Erhardt, M. and Petrick, G. (1989). Relatice concentrations of dissolved fossil fuel residues in Mediterranean surface measure as measured by UVF fluorescence. *Mar. Poll. Bull.* 20: 560-565.

Readman, J.W., Fillmann, G., Tolosa, J., Villeneuve, J.-P., Catinni, C. And Mee, L.D. (2002). Petroleum and PAH contamination of the Black Sea. *Mar. Poll. Bull.* 44: 48-62.

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