

APPLICATION OF ^{252}Cf -PLASMA DESORPTION MASS SPECTROMETRY
TO ANALYSIS OF DIRECT COAL LIQUEFACTION HEAVY PRODUCTS.

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ABSTRACT

Californium Plasma Desorption Mass Spectrometry (PDMS) has been used to analyze heavy distillation residues obtained from direct coal liquefaction processes. The characteristics of the ^{252}Cf -PDMS technique for the analysis of these non-polar materials were determined, especially the ionization efficiency of molecules of different chemical type. The molecular weight distributions of several THF soluble 850°F+ materials ("resids") from the Wilsonville pilot plant were determined. These data were compared to the results obtained by Field Ionization Mass Spectrometry (FIMS) and Gel Permeation Chromatography (GPC). In general, number average molecular weights for all three techniques agreed well. Both GPC and PDMS give higher weight average molecular weights than FIMS and agree with each other for weight averages below 1500 amu.

INTRODUCTION

Field ionization and field desorption mass spectrometry have been applied to the analysis of coal liquefaction products.¹⁻³ ^{252}Cf -PDMS, a different kind of mass spectrometry,⁴⁻⁶ has been incompletely explored for the analysis of coal products.^{7,8}

The ^{252}Cf plasma desorption technique utilizes energetic fission fragments from the decay of ^{252}Cf to volatilize and ionize a solid sample. The ionization source is typically a 10- μCi californium sandwiched between two thin sheets of nickel foil. A sample is dissolved in an appropriate solvent and the solution is electrosprayed over a 1 cm^2 area on an aluminized poly(ethylene terephthalate) foil (Mylar disk). ^{252}Cf -PDMS is capable of producing mass spectra consisting primarily of molecular ions for a wide variety of compounds, including amino acids,⁴ peptides,⁹ nucleotides,¹⁰ geoporphyrins,¹¹ polynuclear aromatic hydrocarbons,¹² polyethers¹³ and other synthetic polymers.¹⁴⁻¹⁶

Gel Permeation Chromatography (GPC), also known as Size Exclusion Chromatography (SEC), has been used to determine the molecular weight distribution of coal extracts.¹⁷⁻¹⁹ The limits of the method and lack of calibration standards for coal derived materials are well known.²⁰ Relative molecular weights values obtained using the same standards (often polystyrenes) and conditions can be satisfactorily compared.

EXPERIMENTAL

Mass spectra were obtained using a BIO-ION 20 commercial time-of-flight mass spectrometer (Bio-Ion Nordic, Upsala, Sweden) equipped with PDP-11 microcomputer data acquisition system (DAS). The instrument is

equipped with 10 μCi ^{252}Cf source and a short 15 cm flight tube. We used a positive 10kV acceleration voltage and the time resolution was set to 1ns/channel. Data collection was terminated at a preset count and 10^6 primary ion events were acquired. This took about 12 minutes. The samples of analyzed distillation resids were dissolved in THF (10 mg/mL) and 40 μl of each solution was electrosprayed onto nitrocellulose coated Mylar disks using the BIO-ION electrospray apparatus. Thin homogenous coverages were obtained. We also developed a software package (CFINT) that can be used on any IBM compatible PC to calculate the number average and weight average molecular weights using data imported from the Bio Ion 20 PDP-11 computer. In addition, this software package allows us to subtract the background spectrum which comes from the mylar film. The software supplied with the spectrometer also adds counts from surrounding channel to enhance the signal-to-noise ratio. This is undesirable for the determination of molecular weight distribution and has been removed from our data analysis.

The molecular weight distributions of five selected resids (#7, #13, #16, #19 and #22) provided by Consolidation Coal Company dissolved in pyridine were measured by a computer interfaced GPC with a mass sensitive detector. The components of the instrument were all commercially available. It consists of a Waters Liquid Chromatograph (Model ALL 201) equipped with high pressure pump, injector, and four μ -styragel columns ($10^4 + 10^3 + 500 + 100 \text{ \AA}$). The mass detector, built by Applied Chromatography Systems Ltd. (Model 750/14), works by nebulizing the liquid stream emerging from the column and then passing this uniform distribution of droplets down a heated tube in a flow of dry nitrogen, evaporating the solvent. The resulting solid passes a light scattering detector whose output is directly proportional to the mass of solid material passing in front of it. Between the mass detector and the columns is a digital thermal pulse flow meter. The outputs from the mass sensitive detector and the flow meter are directed to a Zenith Model 158 microcomputer, the former through a 12 bit resolution A to D converter (Data Translation Model DT 2805). The programs for data collection and manipulation were written in a high level language using the Asyst package (McMillan Software Co.). The instrument was carefully calibrated with polystyrene standards. HPLC grade pyridine was used as the eluting solvent with flow rate of ca. 1 mL/min. 50 μl of each sample with concentration of 10 mg/mL was loaded through the injector valve. For each run data were collected for the period of one hour.

RESULTS AND DISCUSSION

Five THF soluble samples of solid 850°F+ materials ("resids") obtained in the Wilsonville pilot plant during direct liquefaction of different coals were analyzed by ^{252}Cf - Plasma Desorption Mass Spectrometry. Molecular Weight Distribution curves were obtained and number average molecular weights (M_n) and weight average molecular weights (M_w) were calculated. These data are compared to the results obtained by Field Ionization Mass Spectrometry and Gel Permeation Chromatography.

Figure 1 shows the PDMS spectra of Mylar film (a), the software converted spectrum of resid #7 which includes the Mylar background (b), and of resid #7 with the Mylar background subtracted (c). As can be seen only traces of Mylar background remain in the range between 0-100 m/z.

Despite different coal feeds and processing conditions, all the samples show similarities. Table 1 summarize origin and physico/ chemical parameters of the analyzed recycle products. In Table 2. and Fig. 2 (a-c) PDMS results are compared with those obtained from FIMS and GPC. The PDMS M_n values are essentially identical to those from FIMS and GPC. PDMS M_w values are about twice the field ionization results. The FIMS spectra do not show any peaks with molecular weights higher than 1200 - 1300 m/z. Both PDMS and GPC detect molecules having molecular weight greater than 1300 amu. In fact, the PDMS intensity does not return to zero before 2000-2500 m/z. Based on these observations, much higher M_w values can be expected from PDMS and GPC. Probably the field ionization technique is not able to efficiently volatilize high boiling, high molecular weight species. GPC M_w values are higher than the corresponding PDMS results with an exception of resid #19. There are three possible explanations for this phenomenon. 1) The integral of GPC molecular weight distribution curve is very sensitive to small amounts of high molecular weight analytes which are not detected by PDMS. This leads to enormously high M_w values. 2) The recycle oils are fragmenting in PDMS. 3) PDMS is capable of producing mass spectra from a wide variety of natural products but less polar polymeric materials very often give low responses or no peaks at all. PDMS may not be detecting all of the sample.

As can be seen in Table 2, the molecular weights of Resid #19 are much lower than of the other samples. This sample has the highest percentage of condensed aromatics and is low in sulphur and beta and gamma protons (Table1). For this sample PDMS and GPC M_n and M_w values are in overall good agreement. Resids #7, #13 and #22 contain relatively low amounts of condensed aromatics, high numbers of cyclic and alkyl beta and gamma protons, and the highest percentage of oxygen. These resids show higher weight average molecular weights in GPC than in PDMS. The relatively low polarity and highly polymeric nature of these fractions are both unfavorable factors for PDMS. The instrument may not be providing a reliable analysis.

CONCLUSIONS

²⁵²Cf-PDMS is easy to operate, fast and less expensive than most other mass spectrometric techniques and is suitable for quantitative measurements of the molecular weight distributions of some coal conversion products.

Comparison of PDMS molecular weight distributions to the GPC and FIMS shows that, in general, number average molecular weights agree well. Both GPC and PDMS give higher weight average molecular weights than does FIMS.

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REFERENCES

1. Aczel, T.; Laramee, J.; Hansen, G.J. in *Proceedings of the 30th Annual Conference on Mass Spectrometry and Allied Topics*, p.808 (1982)
2. Aczel, T.; Dennis, L.W.; Reynolds, S.D. in *Proceedings of the 35th Annual Conference on Mass Spectrometry and Allied Topics*, p.1066 (1987)
3. Larsen, B.S.; Fenselau, C.C.; Whitehurst, D.D.; Angelini, M.M. *Anal. Chem.* (1986), **58**, 1088
4. MacFarlane, R.D.; Torgeson, D.F. *Science* (1976), **191**, 920
5. MacFarlane, R.D. *Anal. Chem.* (1983), **55**, 1247 A
6. Cotter, R.J. *Anal. Chem.* (1988), **60**, 781 A
7. Lytle, J.M.; Tingey, G.L.; Macfarlane, R.D. *Anal. Chem.* (1982), **54**, 1881
8. Zingaro, R.A.; Macfarlane, R.D.; Garcia, J.M.; Vindiola, A.G.; Zoeller, J.H. in *Chemistry of Coal Liquefaction*, ACS Symposium Ser., Vol. 29, No 5, p. 22 (1984)
9. Alai, M.; Demirev, P.; Fenselau, C.; Cotter R.J. *Anal. Chem.* (1986), **58**, 1303
10. Scanlan, G.; Benson, L.; Tsarbopoulos, A.; Jardine, I. in *Proceedings of the 36th Annual Conference on Mass Spectrometry and Allied Topics*, Denver, CO. (1987), 80
11. Wood, K.V.; Bonham, C.C.; Chou, M.M. *Energy Fuels* (1990), **4**, 747
12. Zoeller, J.H.; Zingaro, R.A.; Macfarlane, R.D. *Int. J. Mass Spectrom. Ion Processes* (1987), **77**, 21
13. Chait, B.T.; Shpungin, J.; Field, F.H. *Int. J. Mass Spectrom. Ion Processes* (1984), **58**, 121
14. MacFarlane, R.D.; McNeal, C.J.; Martin, C.R. *Anal. Chem.* (1986), **58**, 1091
15. Gehrig, C.C.; Wood, K.V. *The 38th ASMS Conference on Mass Spectrometry and Allied Topics* (1990), 255
16. Keough, T.; Lacey, M.P. *Anal. Chem.* (1991), **63**, 1482
17. Larsen, J.W.; Choudry, P. *J. Org. Chem.* (1979), **44**, 2856
18. Larsen, J.W.; Mohammadi, M.; Yiginsu, J.; Kovac, J. *Geochim. Cosmochim. Acta* (1984), **48**, 135
19. Larsen, J.W.; Wei, Y.C. *Energy Fuels* (1988), **2**, 344
20. Buchanan, D.H.; Warfel, L.C.; Biley, S.; Lucas, D. *Energy Fuels* (1988), **2**, 32

Table 1. Analysis of the Soluble Portion of the Distillation Resids

Weight %	Res.#7	Res.#13	Res.#16	Res.#19	Res.#22
	Ill.#6	Tex.Lign.Pitt.#8	Wyodak	Wyodak	
C	88.75	89.39	90.54	90.90	89.46
H	8.15	7.12	6.74	6.32	6.69
N	0.66	1.23	0.91	1.11	1.13
S	0.14	0.09	0.39	0.03	0.05
O	2.30	2.17	1.42	1.64	2.67

Proton Dist.(%)

Cond. Aromatics	16.7	22.4	26.1	32.2	22.5
Uncond. Aromatics	4.4	4.3	5.4	5.1	5.1
Cyclic Alpha	17.9	19.2	18.9	18.1	16.8
Alkyl Alpha	9.4	9.5	9.4	9.2	9.3
Cyclic Beta	18.6	15.9	14.8	13.6	14.4
Alkyl Beta	20.4	18.5	14.6	13.9	21.2
Gamma	12.5	10.3	10.8	7.8	10.8
Phenolic -OH Conc.	0.50	0.71	0.69	0.67	0.89

Table 2. Number Average and Weight Average Molecular Weights Obtained from Field Ionization Mass Spectrometry, Plasma Desorption Mass Spectrometry and Gel Permeation Chromatography.

Resid #	FIMS	PDMS	GPC	FIMS	PDMS	GPC
	M _n			M _w		
7	620	600	600	730	1370	1930
13	570	570	570	680	1340	2050
16	590	590	610	690	1340	1840
19	-	580	500	-	1300	1430
22	-	600	700	-	1460	2160

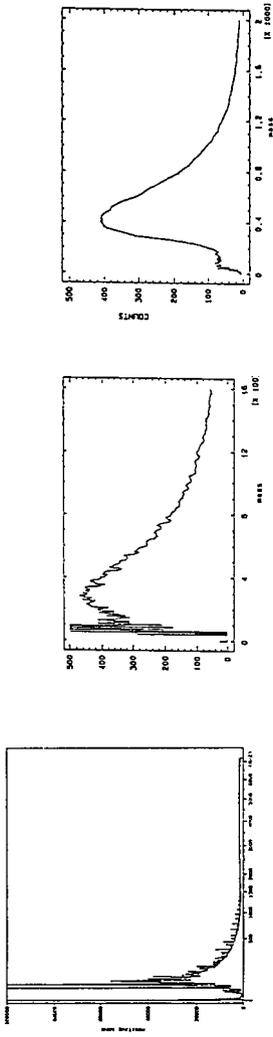


Figure 1. PDMS spectra of Mylar Background (a), Software Converted Spectrum of Resid #7 which include Mylar Background (b) and Resid #7 with Mylar Background Subtracted (c).

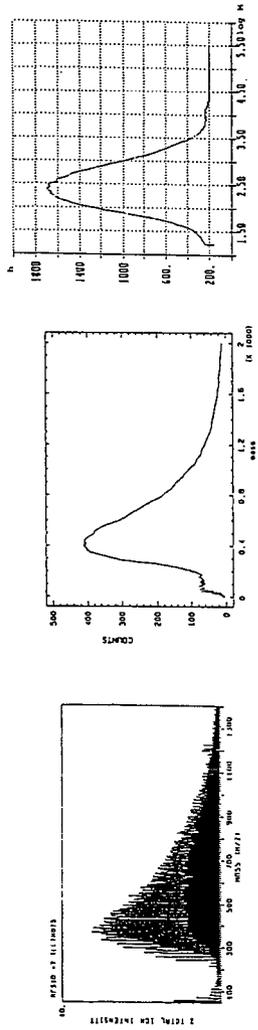


Figure 2. FIMS (a), PDMS (b) and GPC (c) Molecular Weight Distribution of Resid #7