

A large copper block is clamped to the vessel to minimize heating of the sample near the weld.

FURNACE

The furnace used (see Fig. 1) is 25.4 cm (10 in.) high and 15.24 cm (6 in.) in diameter. It has an aluminum oxide tube with a 4.1275-cm (1 5/8-in.) inside diameter, wound with kanthol wire 0.127 cm (0.05 in.) in diameter. The furnace has a maximum temperature range of 1200°C. Two chromel-alumel thermocouples (type K) are used for control and temperature measurement. Bubbled alumina beads are used as filler and insulating material around the heating element. The outside wall is made of aluminum, and the top and bottom ends are of transite. A programmable controller, Data Trak Model 5310, made by Research Inc., Minneapolis, Minnesota, is used to control the heating schedule.

MANIFOLD AND OIL COLLECTION SYSTEM

The gas manifold is designed to use electropneumatic valves and strain-gauge pressure transducers so that the data collection and system operation can be easily automated. To avoid errors in mass balance, the volume of the manifold was kept below 10 cm³. The oil collection is connected to a bellows and to the gas manifold by 0.3175-cm-diameter (1/8-in.) stainless steel tubing. The bellows allows the gases generated in the autogenous atmosphere heatings to flow out of the retort chamber with only moderate pressure changes (67 to 100 kPa, 0.67 to 1 atm). When the gas reaches roughly one atmosphere in the bellows, it is transferred to a 2-l stainless steel collecting bottle.

The oil collector is a graduated, 12-cm³ centrifuge cone, placed inside a glass thimble. A small amount of glass wool is inserted in the top of the thimble to condense any oil mist produced during the assay.

SAMPLE PREPARATION

Sample uniformity directly affects our ability to judge the accuracy of the KSS technique and apparatus and to make comparisons with commercial assay results. We will therefore describe the sample preparation in some detail.

We obtained oil shale from the Anvil Points Mine near Rifle, Colorado. A number of pieces weighing from 4 to 12 kg each were crushed and sieved; material passing a 20-mesh screen (841 μm) was retained and the coarser material was discarded. The density of the 21.0 kg of retained material was 2.28 g/cm³, corresponding to a predicted yield of 88.0 t/t (20.0 gallons/ton). (5) The initial batch was separated into aliquots by a spin riffing technique. (6) The spin riffler is shown in Fig. 3, and the separation scheme is shown in Fig. 4. The first split gave six aliquots weighing about 3.5 kg each. These 3.5-kg aliquots were split into 585-g batches as needed. A third split gave samples of about 95 g each, which were used in the retorting experiments. Four of these 95-g aliquots were sent to Commercial Testing and Engineering Company for Fischer assay.

Two of the 95-g aliquots were split further into 8-g and 0.6-g aliquots for mineral carbonate, total carbon and hydrogen analyses. The results of 12 determinations of total carbon gave 15.97 wt% carbon; σ of a measurement, ± 0.076 ; and 95% confidence limits of the mean, ± 0.048 . We did 49 determinations of acid-evolved CO₂. The results showed 22.19 wt% CO₂, σ of a measurement, ± 0.18 , and 95% confidence limits of the mean, ± 0.05 . The organic carbon calculated from these analyses is 9.914 \pm 0.05 wt%. Organic hydrogen content was uncertain because of the uncertainty in water content.

The unused 3.5-kg and 585-g aliquots were kept in sealed containers so as to exclude air during storage.

PROCEDURE

A 95-g aliquot of oil-shale powder was weighed exactly and placed in the retort chamber. The retort lid was welded to the chamber and the retort reweighed. The retort and sample were then dried at 100°C in a vacuum for 1 h, cooled to room temperature, and reweighed. (Typical weight loss due to drying was 0.23% of sample weight.) All of the components of the product-collection systems were then weighed, and the retort was placed in the furnace and connected to the collection system and manifold setup. The furnace openings were lightly plugged with insulating material (Fiberfrax). The system was then evacuated, checked for leaks, and backfilled with argon to a pressure of 67 kPa (0.67 atm). The sample was then heated in the Fischer assay mode (12°C/min to 500°C, with a final holding period of 30 min at 500°C). (3,4) After the system had cooled, the weights of all products (gas, oil, and water) were determined. The oil collector was centrifuged to separate the oil and water phase. Most of the oil was removed with a pipette, and the oil remaining with the water phase was extracted with benzene followed by hexane. The hexane was allowed to evaporate, and the weight of the water was determined. The water phase was then discarded.

The spent shale was spin-riffled into aliquots, one of which was analysed for C, H, N, and S. Oil density was determined using a 3-cm³ pycnometer. An oil aliquot was taken for analyses, and the remainder was stored at 0°C under argon. The product gas was weighed and then analysed by mass spectrometry. The gas mass was corrected for the initial amount of argon and the amount of gas remaining in the retort-bellows system. We found this correction to be trivial.

An overall material balance was calculated by comparing the weight loss during heating to the total mass of the products collected. Typically, the results ranged from 99.0 to 101.0%. If the spent shale is counted as a product, the material balance results will range from 99.9 to 100.1%. A typical run sheet is shown in the appendix.

RESULTS AND DISCUSSION

EXPERIMENTS IN THE FISCHER ASSAY MODE

The results of our assays in the Fischer assay mode are summarized in Tables 1 and 2. The mass yields, in kg/t, were measured directly. The volume yields, in gal/ton, were calculated from the mass yields via:

$$\text{Yield}_{(\text{vol})} \text{ gal/ton} = \text{Yield}_{(\text{mass})} \frac{\text{kg}}{\text{t}} \times \frac{0.239653 \text{ gal}\cdot\text{t}\cdot\text{g}}{\rho \text{ g/cm}^3 \text{ ton}\cdot\text{kg}\cdot\text{cm}^3} \quad (1)$$

The volume yield depends on the oil density, which in turn depends on the temperature. We normally measure oil densities at 21°C (70°F). Since the oil industry reports densities at 15.6°C (60°F), we measured several oils at both 21°C and 15.6°C and found the densities to be 1% higher at 15.6°C. The 15.6°C densities listed in Table 1 are calculated values.

The results from the four commercial Fischer assays are listed in Table 3. To compare the commercial assay values with our work, we calculated mass yields from the reported volume yields and densities. We assumed that both values were measured at the same temperature.

Our work gave a mean yield of 84.07 kg/t and the commercial results gave 83.25 kg/t. Using the "t" test (7) of significance between two sample means and the standard deviation of the measurement shown in Table 1, we can determine

that there is a 60% probability that the two assay values are the same.

The uncertainty in our KSS assay procedure for a single determination is about 1.2%. The uncertainties in the total carbon and acid-evolved CO₂ are 0.5% and 0.8%. We believe that the analytical procedures are more precise than these numbers imply, and that the major contribution to statistical scatter comes from the spinning technique used in sampling.

J. Ward Smith (3) reported σ of $\pm 0.3\%$, and 95% confidence limits of the mean of $\pm 0.3\%$ in his paper on Fischer assay procedures. Goodfellow and Atwood (4) reported 95% confidence limits of 0.8 to 1.6% on a series of assays. Furthermore, they state, "Our experience has been that most problems with precision and accuracy can be traced to inadequate sample preparations procedures." We certainly agree. The results discussed above are summarized in Fig. 5.

The oils from our assays were analysed for C, H, N, and S. Although we did not attempt to carry out a complete elemental balance as did Smith, (3) it is interesting to compare our products with his work and with the work of Goodfellow and Atwood. (4) Our oil had a composition of CH_{1.63}N_{0.02}S_{0.003}. Smith's oils were CH_{1.55}N_{0.02}S_{0.003}. Our data on the distribution of organic carbon among the products (oil, char, and gas) were also slightly different from those of Smith (3) and of Goodfellow and Atwood. (4)

The organic carbon originally present in the shale (9.914 wt%) was distributed 73.2% in oil, 19.7% in char, and 7.1% in gas (by difference). Smith's distribution was 66% in oil, 23.5% in char, and 10.5% in gas. Goodfellow and Atwood reported 64.6% in oil, 24.6% in char, and 11% in gas (by difference).

In 1974, Cook (8) reported correlations between elemental analysis of raw shales and Fischer assay yields for 152 samples of Green River oil shale, and our oil yield, in wt%, calculated from the organic carbon content of the raw shale, falls within the uncertainty limits of Cook's correlation.

USE OF KSS RETORT APPARATUS FOR NONROUTINE RESEARCH

Beyond routine Fischer assays, the apparatus described above is versatile enough to handle a variety of unique experiments. We have recently reported a series of experiments (2) on the effects of long-term heat soaking on oil yield from powdered shale samples. Heating times ranged from 8 to 800 h and temperatures up to 400°C. In some cases, a controlled sweep of inert gas was used. In all experiments, the KSS apparatus was used, and it gave excellent material balances (see Ref. 2 for results).

Using a nonisothermal technique, (9) we have also made a kinetic study of oil production. Comparing the results of this study with those from a number of other isothermal experiments, we found excellent agreement. In these kinetic studies, we were able to use the KSS apparatus without any modifications, and the kinetic experiment simulated the real in-situ condition (nonisothermal heating).

More recently, we have completed studies on the effects of different heating rates and gas sweep atmospheres on oil yield from powdered oil shale in 1-in. cores. (2) Again, the KSS apparatus was used without modification. The results of this last investigation give insight into the mechanism of oil degradation during long-term in-situ retorting experiments.

CONCLUSIONS

We have designed, built, and tested a simplified laboratory retort system (KSS apparatus) that simulates conditions involved in in situ oil shale processing.

The apparatus is of simple design, and it can be used with commercially available cylindrical furnaces. The welded closure is rugged and leak-tight. When operated in the Fischer assay mode, our apparatus gives results indistinguishable from those of a Fischer assay. The KSS apparatus is versatile. It can provide excellent mass balance in a wide variety of retorting experiments. Various sweep gases can be used. The heating schedule is completely programmable, and the apparatus can run unattended for long periods (> 1 month).

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REFERENCES

1. A. E. Lewis and A. J. Pothman, Rubble In-Situ Extractions (RISE): A Proposed Program for Recovery of Oil From Oil Shale, Lawrence Livermore Laboratory, Rept. UCRL-51768 (1975)
2. N. D. Stout, G. J. Koskinas, T. H. Paley, S. D. Santor, R. J. Opila, and A. J. Rothman, Pyrolysis of Oil Shale: The Effects of Thermal History on Oil Yield, Lawrence Livermore Laboratory, Rept. UCRL-77831 (1976)
3. J. W. Smith, Analytical Method for Study of Thermal Degradation of Oil Shale, U.S. Bureau of Mines Report of Investigations, No. 5932 (1962)
4. L. Goodfellow and T. Atwood, Col. Sch. Mines Quart. 69 (2), 205 (1974)
5. J. W. Smith, Chem. Eng. Data Ser. 3, 306 (1958)
6. C. A. Slettevold and A. H. Biermann, Characterizations of ASTM Round-Robin Tungsten-Powder Samples, Lawrence Livermore Laboratory, Rept. UCRL-51812 (1975)
7. E. L. Bauer, A Statistical Manual for Chemists, Academic Press, New York, (1971)
8. E. W. Cook, Fuel 53, 16 (1974)
9. J. H. Campbell, G. Koskinas, and N. Stout, The Kinetics of Decomposition of Colorado Oil Shale: 1. Oil Generation, Lawrence Livermore Laboratory, Rept. UCRL-52089 (1976)

TABLE 1

KSS Assay Results

SAMPLE NO. ^a	MATERIAL BALANCE (%)	YIELD (kg/t)	YIELD ^b (gal/t)	DENSITY (g/cm ³)	
				at 21 ^o C	at 15.6 ^o C ^c
(4-5)-4	-	84.98	22.2 ^d	-	-
(1-1)-4	-	85.33	22.3 ^d	-	-
(1-6)-1	98.6	83.67	22.3	0.890 ^e	0.899
(4-5)-5	101.4	83.44	22.0	0.900 ^e	0.909
(1-5)-1	98.9	83.25	21.9	0.903	0.912
(1-6)-6	101.0	85.44	22.4	0.908	0.917
(4-6)-2	99.9	82.56	21.5	0.912	0.921
(1-6)-2	99.8	84.09	21.9	0.912	0.921
(4-6)-4	99.6	83.27	21.7	0.908	0.917
(1-3)-6	100.7	84.68	22.2	0.905	0.914
Mean Value		84.07	22.0	0.908	0.917
σ of a Measurement		0.99	0.3		
95% Confidence Limits of the Mean		0.71	0.2		

^aSample numbers refer to the sample-splitting scheme shown in Fig. 4.

^bYield in gal/ton calculated at 15.6^oC from mass yield and density.

^cDensity at 15.6^oC = density at 21^oC (measured) x 1.01.

^dYield in gal/ton calculated using mean density, 0.917 g/cm³.

^eDensity estimated by visual measurement of oil volume; not used in calculation of mean density.

TABLE 2

Analytical Summary

Sample	Elemental Analysis, wt%						% of Original Organic Carbon Present
	Total Carbon	Organic Carbon	Hydrogen	Nitrogen	Sulfur	Oxygen	
Raw Shale	15.97	9.914	1.43	0.34	0.14	-	100
Spent Shale	8.84	2.19	0.19	0.17	0.15	-	19.7
Oil	86.38	86.38	11.22	2.06	0.67	-	73.2
Gas ^a	57.9	57.9	12.3	-	-	29.8	7.1 (by difference)

^a24.2 vol % CO₂; 26.1 vol % H₂; 18.4 vol % CH₄; $\sum_n C_n = 25.9$ vol % (average composition for $\sum C_n = C_{3.2} H_{7.5}$)

TABLE 3

Results of Fischer Assay
Performed by Commercial Testing and Engineering Co.

Sample No. ^a	YIELD ^b (kg/t)	YIELD (gal/t)	DENSITY ^c (g/cm ³)
(1-1)-3	84.02	22.2	0.907
(1-1)-5	83.05	21.8	0.913
(4-5)-2	82.78	21.8	0.910
(4-5)-6	83.16	21.9	0.910
Mean Value	83.25	21.9	0.910
σ of a Measurement	0.54	0.2	
95% Confidence Limits of the Mean	0.85	0.3	

^aSample numbers refer to the sample-splitting scheme shown in Fig. 4

^bYield in kg/t calculated from volume yield and density

^cDensity measurement at an unknown temperature - see text

APPENDIX: Typical Material Balance Sheet for Oil Yield Experiments
(Fischer Assay Heating Schedule)

Item	Weight (g)
1. Retort and lid	296.5312
2. Tare and sample	227.3068
3. Tare	125.5600
4. Sample (2 - 3)	101.7468
5. Assembled full retort (1 + 4)	398.2780
6. Assembled and welded retort before drying	398.2472
7. Weight change due to welding (5 - 6)	0.0308
8. Assembled and welded retort after drying	397.9693
9. Weight loss due to drying (6 - 8)	0.2779
10. Weight of retort after heating	386.8700
11. Weight loss on heating (8 - 10)	11.0993
12. Collection tube, oil, and water	27.2546
13. Collection tube and water	19.5628
14. Collection tube (clean)	18.8655
15. Weight of water (13 - 14)	0.6973
16. Weight of oil (12 - 13)	7.6918
17. Thimble, glass wool, and oil	74.4964
18. Thimble and glass wool (clean)	73.6902
19. Oil in thimble (17 - 18)	0.8062
20. Downspout, stopper, and oil	25.3609
21. Downspout and stopper (clean)	25.3030
22. Oil in downspout (20 - 21)	0.0579
23. Total oil collected (16 + 19 + 22)	8.5559
24. Gas bulb (full)	919.4503
25. Gas bulb (evacuated)	917.6485
26. Gas collected (24 - 25)	1.8018
27. Gas correction	0.0312
28. Total product collected (26 + 27 + 23 + 15)	11.0862
29. Pycnometer and oil	28.9494
30. Pycnometer (clean)	26.2119
31. Oil density, g/cm ³ [(29 - 30)/3.0 cm ³]	0.9125
32. Material balance, % (28 x 100/11)	99.88
33. Oil yield, kg/t (23 x 1000/4)	84.0901
34. Oil yield, gal/ton (33 x 0.239653/31)	22.085

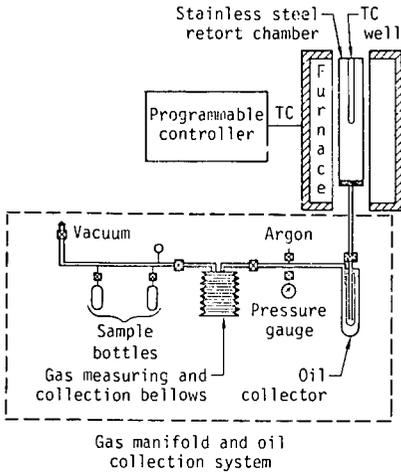


Fig. 1. Schematic of the KSS oil shale assay apparatus.

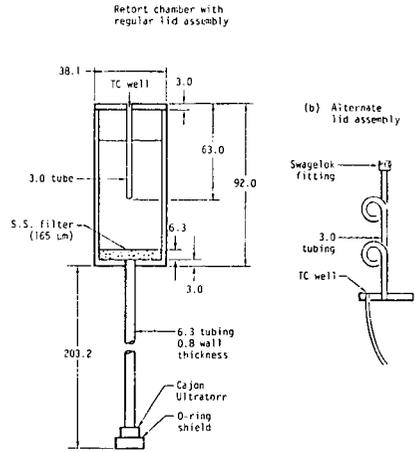


Fig. 2. Retort chamber assembly (dimensions in mm).

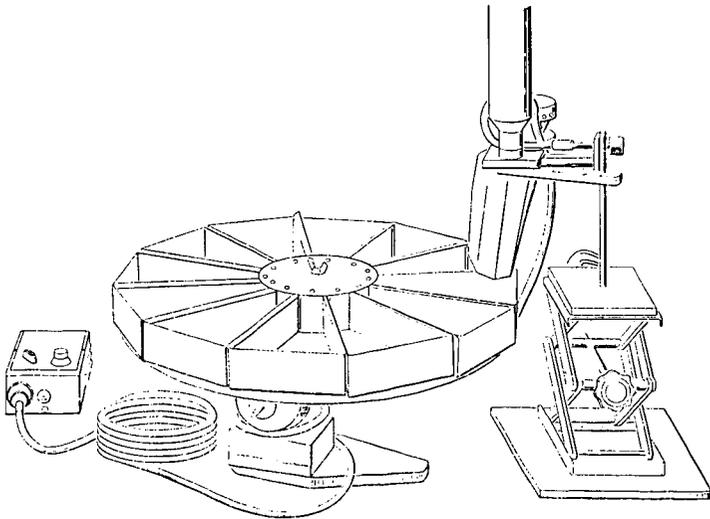


Fig. 3. Spin-riffing apparatus.

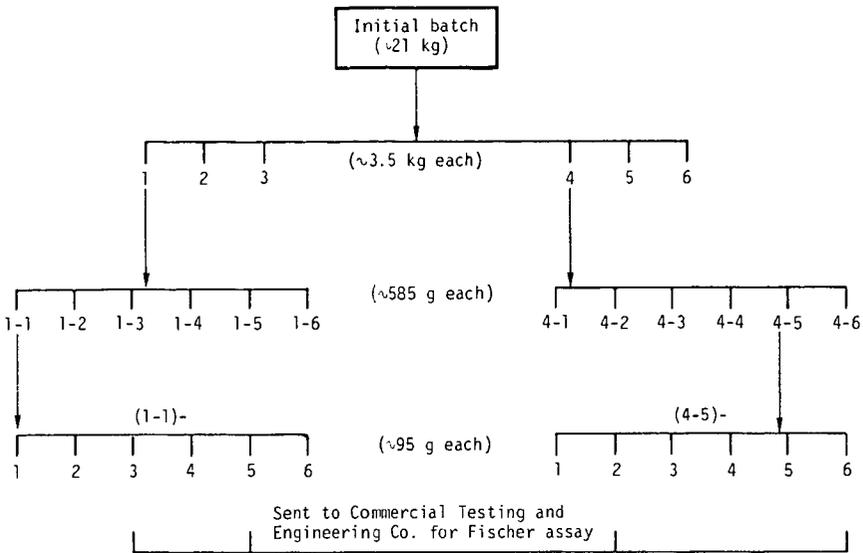


Fig. 4. Sample-separation flow chart.

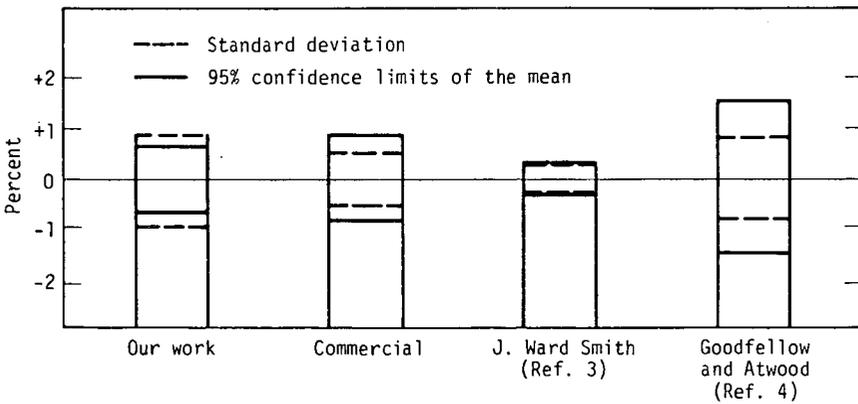


Fig. 5. Comparison of the accuracy of assay results from various sources.