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INTERLABORATORY, MULTIMETHOD STUDY OF AN IN SITU PRODUCED OIL SHALE PROCESS WATER

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INTRODUCTION

Accurate measurement of chemical constituents in waters from alternative fossil energy sources, such as oil shale, is essential to the orderly and timely development of those energy resources. The technology necessary to handle, contain, treat, utilize, and dispose of those waters and the information needed to predict their environmental effects and to determine regulatory compliance, require careful chemical characterization. This is particularly important for in situ oil shale technologies because about 1 barrel of water may be coproduced with each barrel of oil.[1]

Reliable chemical characterizations of synfuel process waters have been difficult to obtain. This is due to the lack of adequate standards and limitations of many available analytical methods. Concentrations of many constituents fall outside the recommended ranges for published methods, or chemical interferences produce inaccurate results. These problems have been identified by many researchers faced with making chemical measurements.[2-5] They were first nationally acknowledged when the ASTM Committee on Water, D-19, formed Subcommittee D-19.33 on "Water Associated with Synthetic Fuel Production" to address analytical problems specific to alternative fossil energy process waters.

The purpose of the present work was to obtain a careful chemical characterization of an oil-shale process water designated for wide use in environmental research and to determine the suitability of existing analytical methods for this characterization. The study was carried out

using an interlaboratory, multimethod approach. Samples from a larger volume, homogeneous reserve of an in situ oil-shale process water were prepared and submitted to 13 laboratories for the measurement of major, minor, and trace elements and standard water quality parameters; a variety of instrumental and chemical methods was used. This paper presents the characterization of that water and discusses analytical problems specific to in situ oil-shale process waters.

In Situ Oil-Shale Process Water

Water coproduced with shale oil and decanted from it is referred to as oil-shale process water. This water originates primarily from three sources: combustion, dehydration of minerals, and groundwater.[1] The ratio of water to oil ranges from 0.15 to 22, depending on the retorting atmosphere (air or inert gas) and the geographical location of the oil shale reserve.[1] This paper considers an air atmosphere process (combustion) and the oil shale reserves near Rock Springs, Wyoming.

Simulated in situ oil-shale process waters produced in laboratory-scale and pilot-scale retorts have been characterized by several investigators.[2-7] Large variations in many measured parameters have been noted.[3,5,7] These waters are brown to yellow in color, have a pH that ranges from 8.1 to 9.4, and contain high levels of inorganic and organic constituents. The primary inorganic constituents are HCO_3^-, $SO_4^=$, $S_2O_3^=$, SCN^-, F^-, Mg^{++}, Na^+, K^+, and NH_4^+.[7] The organic constituents are primarily polar and the carboxylic acids are a major organic group.

OMEGA-9

The oil-shale process water used in this work is from the 1976 Rock Springs Site 9 true in situ oil shale combustion experiment conducted by the Laramie Energy Technology Center (LETC).[8] This water has been designated "Omega-9" (Ref. 9) and that descriptor will be used in this paper. The chemical composition of this sample is specific only to itself and is not necessarily representative of in situ oil-shale waters in general. Nevertheless, the analytical problems encountered in the analysis of this sample are typical of these waters due to a common matrix that includes high levels of inorganic and organic N, S, and C compounds.

Preparation

The acquisition, processing, and storage of Omega-9 are discussed in detail by Farrier et al.[9] Briefly, 12,450 gal of process water were collected from a storage pond after 1 to 3 days residence; mixed, to ensure homogeneity, by pumped recirculation through a storage vessel; and pressure-filtered in the field through two in-line cartridge-type membrane filters with a nominal 0.4-μm exclusion. The materials in direct contact with the sample were either an inert epoxy coating, inert plastic, or stainless steel. The filter cartridges were constructed of polypropylene. The upstream filter material was a compressed matrix of borosilicate micro-fiberglass with an acrylic resin binder, and the downstream filter was cellulose esters cast onto a cellulose web. The filtered sample was

partitioned into 415 polyethylene-lined, 30-gal drums and stored at 4°C. Each laboratory participating in the study received a 500-ml sample from one of four of these drums.

Homogeneity

The homogeneity of the resulting sample with respect to some of the parameters evaluated in this study was investigated by randomly selecting three 30-gal drums for detailed analysis. Aliquots from each drum were analyzed for representative major, minor, and trace elements and water quality parameters by two participating laboratories using techniques of known high precision. The results of those analyses are summarized in Table 1. The entries in Table 1 are average concentrations plus or minus 1 standard deviation. The number of analyses included in the average is shown in the second column. All parameters for each barrel agree to within 2 standard deviations. These data suggest that Omega-9 is homogeneous.

Stability

Stability of oil-shale process waters is a significant concern. Most researchers have noted that samples stored at >4°C to 40°C develop considerable turbidity after several days. This turbidity is composed primarily of stressed rod-shaped bacterial cells.[9] These cells have a large adsorptive capacity and, within 10 days, remove significant amounts of the elements Br, Se, As, Fe, Ni and Hg from filtered samples stored at room temperature.[5]

The stability of Omega-9 water with respect to these visual changes, microbial growth, and organic content was investigated by Farrier et al.[9] and Felix et al.[10] The work of Refs. 9 and 10 indicated that storage at 4°C stabilized the water's organic content by inhibiting microbial growth. Therefore, the loss of chemical constituents due to adsorption on bacterial cells would also be significantly lessened.

An additional concern with aqueous samples is the loss of constituents by adsorption onto container walls or precipitation reactions. These effects are usually minimized by acidifying the sample to pH < 2 with concentrated HNO_3.[11-13] Such acidification was not possible in this case. The sample is highly buffered by the $CO_3^{=}$ and NH_3 systems and contains high levels of $S_2O_3^{=}$. Acidification results in the precipitation of elemental S and organic acids. The precipitates act as adsorbents for some elements, interfere with most analytical measurements, and result in an inhomogeneous sample. Because the sample is well buffered, relatively large volumes of acid are required; as a result, the acid further dilutes many low-level constituents, and may contaminate the sample.

Stability of Omega-9 water for select major, minor, and trace elements was investigated by several participating laboratories. No change was noted in elemental content on storage in polyethylene-lined containers for up to 1 year at 4°C.

Table 1. HOMOGENEITY TEST OF OMEGA-9 (mg/ℓ except as noted)[a]

Parameter	Number of Measurements	Barrel 1	Barrel 2	Barrel 3
ELEMENTAL ANALYSES[b]				
Antimony (NAA)	1	2.02 ± 0.05	2.03 ± 0.05	2.03 ± 0.05
Calcium (AAS)	1	20.3 ± 0.3	19.2 ± 0.3	16.9 ± 0.3
Copper (AAS)	1	0.09 ± 0.03	0.07 ± 0.03	0.04 ± 0.03
Iron (AAS)	1	1.70 ± 0.20	1.49 ± 0.20	1.49 ± 0.20
Lithium (AAS)	1	0.19 ± 0.01	0.18 ± 0.01	0.18 ± 0.01
Magnesium (AAS)	1	22.2 ± 0.2	21.9 ± 0.2	22.2 ± 0.2
Silicon (AAS)	1	5.2 ± 0.7	5.2 ± 0.7	5.2 ± 0.7
Silver (AAS), μg/ℓ	5	2.74 ± 0.59	3.42 ± 0.38	2.79 ± 0.35
Sodium (AAS)	1	4400 ± 100	4200 ± 100	4300 ± 100
Zinc (AAS)	1	0.30 ± 0.01	0.35 ± 0.01	0.30 ± 0.01
WATER QUALITY PARAMETERS				
Alkalinity, total (as $CaCO_3$)	1	16,900	16,900	16,000
Carbon, inorganic	3	3650 ± 365	3630 ± 365	3790 ± 380
Carbon, organic	3	1050 ± 210	1310 ± 260	1032 ± 210
Chemical oxygen demand	1	4935	5120	5105
Electrical conductivity (μmhos/cm)	1	25,200	25,600	23,500
pH	1	8.80	8.80	8.86

[a]Note: Indicated errors are one sigma for replicate analyses. If a single measurement is reported, the error is counting statistics (NAA) or signal background (AAS).

[b]NAA = neutron activation analysis; AAS = atomic absorption spectroscopy.

EXPERIMENTAL

A 500-ml aliquot of Omega-9 water, contained in an opaque plastic container, was sent to each of the 13 participating laboratories. Laboratories were selected to provide a mix of research-grade analyses, such as those performed at Department of Energy national laboratories, and routine analyses, such as are available at many commercial establishments. Most laboratories selected had prior in-depth experience analyzing a wide variety of environmental samples, including oil shale materials. The participating laboratories were coded to maintain anonymity.

Six instrumental methods were selected for detailed elemental analyses: neutron activation analysis (NAA); X-ray fluoresence spectrometry (XRF); spark source mass spectrometry (SSMS); optical emission spectroscopy (OES); plasma emission spectroscopy (PES); and atomic absorption spectroscopy (AAS). Sample preparation techniques and the suite of elements measured were left to the discretion of each laboratory. Reported results include uncertainties due to both the analysis itself and the method of sample preparation.

The measured water quality parameters include alkalinity, biochemical oxygen demand (BOD_5), $CO_3^{=}$, HCO_3^{-}, organic and inorganic C, conductivity, CN^-, hardness, NH_3, NH_4^+, $NO_3^{=}$, organic N, Kjeldahl N, oil and grease, pH, phenols, $PO_4^{\equiv}$, solids, chemical oxygen demand (COD), and S species. The best analytical method and sample pretreatment were left to the discretion of each laboratory. In most cases, Standard Methods[11] or EPA Methods[12] were used.

The instrumental and chemical methods used to measure major, minor, and trace elements and water quality parameters in Omega-9 water are summarized in Tables 2 and 3. Additional information is available in Ref. 7.

RESULTS

The detailed analyses of major, minor, and trace elements are presented in Table 4, and of water quality parameters in Table 5. Inspection of these data indicates that there is a wide spread in values for many elements and water quality parameters. Therefore, a statistical technique[32] was used to provide a basis for discarding outlying values. The result of applying this technique to the individual values in Tables 4 and 5 is summarized in Table 6. This table presents the best value, in the judgment of the authors, for 72 elements and 28 water quality parameters.

The procedure used to analyze the data was as follows. Measurements made using a technique with known interferences were discarded. These are documented in the footnotes to Table 6. Dixon's technique was then applied to the remaining data to reject outliers.[32] This method expresses the gap between an outlier and the nearest value as a fraction of the range from the smallest to the largest value. The value of this fraction provides the basis for rejection. A range was reported when the coefficient

Table 2. SUMMARY OF INSTRUMENTAL METHODS USED FOR THE ANALYSES OF OMEGA-9

Instrumental Technique	Laboratory	No. of Replicates	Sample Preparation	Special Features	Elements Detected
NAA	A	1	Evaporation at 80°C	2 irradiations and 5 decay/counting measurements	Sb, As, Ba, Cs, Cl, Co, Hf, Fe, Mo, Ni, Rb, Sc, Se, Ag, Na, Th, U, Zn
NAA	B	2	Direct analysis of liquid	2 irradiations and 5 decay/counting measurements	Al, Sb, As, Br, Cl, Sc, Se, Na
NAA	C	1	Direct analysis of liquid	2 irradiations and 3 decay/counting measurements	Sb, As, Br, Cl, Co, Cu, Mn, Mo, Na, U
NAA	D	3	Direct analysis of liquid	1 irradiation and 3 decay/counting sequences	Sb, As, Br, Cl, Co, Fe, Sc, Se, Na, Sr, U, Zn
XRF	A	3	Freeze dried	energy-dispersive system with Mo x-ray tube; counted for 20 min	As, Br, Ca, Cu, Fe, Mn, Ni, Rb, Se, Sr, Ti, U, V, Zn, Zr
XRF	B	3	Air dried	energy-dispersive system with Ag secondary source; counted for 100 min	As, Br, Ca, Cu, Mo, Rb, Se, Zn, Zr
XRF	N	1	Direct analysis of liquid	wavelength-dispersive system with Pt x-ray tube; counted for 100 sec	Cl
SSMS	E	2	Carbon slurry dried with infra-red lamp	m/e fractions analyzed by ion-sensitive photo-plates and the disappear-ing line technique	Al, Sb, As, Ba, Br, Cd, Cs, Cr, Co, Cu, Ga, Ge, Hf, I , Fe, La, Pb, Mn, Mo, Ni, Nb, P, Pr, Rb, Se, Si, Ag, Sr, Ta, Te, Sn, Ti, W, U, V, Y, Zn, Zr
PES	D	3	Direct analysis of liquid	System used Ar plasma jet and Echelle grating spectrometer	As, Ba, B, Ca, Cu, Mg, Mo, P, Si, V, Zn
OES	F	1	Evaporation, ignition at 450°C and grinding	D.C. arc source coupled to grating spectrographs	Sb, Ba, B, Cr, Co, Fe, Pb, Li, Mn, Mo, Rb, Sr, Ti, V, Zr
AAS	A	3	Direct analysis on liquid except Hg which was evaporated at 80°C	Zeeman AAS; graphite rod atomization	As, Se, Cd, Ag, Hg
AAS	C	2	Digestion; Ref. 14	flame atomization; corrections for matrix effects	Ca, Mg, Na, K, Fe, Si, As, Se, Sb
AAS	D	3	Ref. 15	flame atomization; correction for Na matrix	Na, Mg, Si, Fe, Li, Ca, Cu, Zn
AAS	E	2	Ref. 12, 16	flame atomization except K, Na by flame emission	Ca, K, Mg, Na, Hg
AAS	F	1	Ref. 12	flame atomization	Na, K, As, Se, Hg, Zn, Ca, Mg, Al
AAS	G	1	Ref. 12, 17	flame atomization	Na, K, Ca, Mg, Se, Pb, Cd
AAS	H	3-10	Ref. 15, 18	flame atomization	Mn, Ni, Zn, K, Fe, Ca, Sn
AAS	I	2	Ref. 19	flame atomization; correction for Na matrix	Ca, Mg

Table 3. SUMMARY OF CHEMICAL METHODS USED FOR THE ANALYSIS OF OMEGA-9

Chemical Parameter	Laboratory	Method	Interferences	Reference
Alkalinity	A, F, J, N	Titrimetric	Soaps, oils	11, 12
Arsenic	N	Ag diethyldithiocarbonate	Co, Hg, Ni, Ag, Cu, Cr, Mo, Sb	11
BOD_5	F	5 day incubation	Various toxicants	12
Boron	C	Dianthrimide method	Unknown	–
	I	–	Unknown	14
	E	–	Unknown	11
Calcium	J	EDTA titrimetric	$PO_4^{\equiv}$, Ba, Sr, alkalinity	11
Carbon (HCO_3^-, $CO_3^{\equiv}$)	C, F, H, I, K	Computed from alkalinity	NH_3, B, Si, organic bases	11, 12
Carbon, inorganic	A, C	–	Unknown	11
	H	–	Unknown	20
Carbon, organic	K, C	Sealed ampoule	Unknown	–
	H, M, N	Direct	Volatile organics	11
	A	Indirect	Unknown	11
COD	A, F, J, I	Chemical oxidation	$S_2O_3^{\equiv}$, $S_4O_6^{\equiv}$	11,12
	N	Chemical oxidation	$S_2O_3^{\equiv}$, $S_4O_6^{\equiv}$	21, 22
Chloride	F, H, J	$Hg(NO_3)_2$ titration	Organics, I^-, Br^-	11, 12
	E	–	–	23
	C, I	Technicon Autoanalyzer	Br^-, I^-, SCN^-	12
Conductivity	A, G, I	Instrumental	Soaps, oil, grease	11, 12
Cyanide	F	Colorimetric	Color	12
	C, N	Distillation/specific ion electrode	Fatty acids	11
Fluoride	D, E, F, G, N	Specific ion electrode	Unknown	11, 12
	C	Technicon Autoanalyzer/ specific ion electrode (C) or Technicon Autoanalyzer (N)	Unknown	–
	I	SPADNS	Unknown	12
Hardness	H	EDTA titration	Unknown	11
	I	Computed	–	–
Magnesium	J	Computed	See Ca, hardness	11
Nitrogen, ammonia	A, H, J	Distillation/titrimetric	Amines	11
	C	Distillation/idophenol	Unknown	12
	J, N	Specific ion electrode	Amines	12, 24
Nitrogen, Kjeldahl	C	Technicon Autoanalyzer	Unknown	–
	F, H, I	Distillation	Amines plus others excluded	11, 12, 25
Nitrogen, organic	J	Distillation/titrimetric	Amines plus others excluded	11
	H	Computed	Amines plus others excluded	–
Nitrogen, nitrate	F	Colorimetrically	SCN^-	12
Oil and grease	C	Freon extraction	Organics	12
pH	A, C, F, G, H, I, J, N	Electrometrically	Soaps, oils, grease	11, 12
Phenols	A, C, F, J, N	Colorimetrically	Para-substituted phenols	11, 12
Phosphorus, orthophosphate	J	Stannous chloride	SiO_2, As, F^-, $S_2O_3^{\equiv}$, SCN^-	11
	F	Colorimetrically	Unknown	12
Phosphorus, total	C, F	Technicon Autoanalyzer	Unknown	12
Potassium	I	Technicon Autoanalyzer	Unknown	–
Silicon	I	–	Unknown	14
Sodium	I	Technicon Autoanalyzer	None known	–
	J	Specific ion electrode	Unknown	–
Solids	A, F, G, H, I, J, N	Gravimetric	NH_3, NH_4^+, HCO_3^-, $CO_3^{\equiv}$	11, 12
Sulfur, sulfate	A, C, F, J	Turbidimetric	None known	11, 12
	G, N	Gravimetric	None known	12
	I	Chloranilate	None known	12
Sulfur, sulfide	A, N	Titrimetric	S compounds, volatile organics	12, 26
	C	Qualitative	None known	11
Sulfur, sulfite	F	Titrimetric	Organics	12
Sulfur, thiocyanate	A, C	Colorimetric	None known	11
Sulfur, tetrathionate	C	Colorimetric	Unknown	27, 28
Sulfur, thiosulfate	C	–	Unknown	27, 28
	J	Titrimetric	Unknown	–
Sulfur, total	C	Digestion	Unknown	29
	E, H	Gravimetric	None known	30
Uranium	G	–	None known	31

Table 4. ELEMENTAL ANALYSIS OF OMEGA-9 (mg/ℓ)

Element	Instrumental Methods[a]: X-ray Fluorescence Spectrometry		Instrumental Neutron Activation Analysis				Spark Source Mass Spectrometry	Emission Spectroscopy		Atomic Absorption Spectroscopy	Chemical and other Methods[a]	Element
								Optical	DC Plasma			
	A	D	B	C	D	A	E	F	D			
Aluminum	–	–	19.1±4.1	–	–	<420	0.30±0.06	–	<0.03	<1[F], 1[H]	–	Aluminum
Antimony	–	–	1.81±0.36	1.81	2.03±0.03	1.66±0.16	2.6±0.7	1.0±0.1	–	2.5[C]	–	Antimony
Arsenic	0.92±0.02	1.09±0.02	0.84±0.18	0.88	1.17±0.03	1.3±0.3	0.58±0.08	–	1.0±0.2	1.0±0.1[A], 1.1[C], 1.3[F]	0.7[N]	Arsenic
Barium	0.63±0.17[b]	–	< 4.4	–	–	0.41±0.24	1.1±0.0	1.0±0.1	0.39±0.04	<10[H]	–	Barium
Beryllium	–	–	–	–	–	–	<0.002	<0.01	–	–	–	Beryllium
Bismuth	–	–	–	–	–	–	<0.004	<0.01	–	–	–	Bismuth
Boron	–	–	–	–	–	–	–	40±4	23±1	30[H]	22[C], 22±0[E], 26[I]	Boron
Bromine	2.70±0.08	2.44±0.1	2.07±0.42	3.0	2.65±0.09	–	1.8±0.0	–	–	–	–	Bromine
Cadmium	–	–	< 3.3	–	–	<0.8	0.001±0.000	–	<0.01	0.0022±0.0001[A], <0.1[G]	–	Cadmium
Calcium	12.4±0.6	7.5±1.4	<410	–	–	<2200	–	–	7.3±0.4	c	16.3[J]	Calcium
Cerium	–	–	< 0.23	–	–	<0.026	–	–	–	–	–	Cerium
Cesium	–	–	< 0.045	–	–	0.0021±0.0003	0.004±0.001	<0.01	–	–	–	Cesium
Chlorine	–	–	793±160	895	870±40	741±35	–	–	–	–	d	Chlorine
Chromium	<0.10	–	< 0.24	–	<0.06	<0.02	0.019±0.000	0.02±0.002	–	–	–	Chromium
Cobalt	<0.27	–	< 0.091	0.028	0.020±0.003	0.022±0.001	0.028±0.000	0.05±0.01	–	<0.1[G]	–	Cobalt
Copper	0.13±0.10	0.17±0.07	<90	0.075	–	<5	0.09±0.04	<0.01	0.04±0.03	0.07±0.03[D], 0.1[G]	–	Copper
Dysprosium	–	–	< 0.18	–	–	<0.04	<0.002		–	–	–	Dysprosium
Europium	–	–	< 0.049	–	–	<0.0013	<0.002	–	–	–		Europium
Fluorine	–	–	<3300	–	–	–	–	–		–	e	Fluorine
Gallium	<0.021	–	<17	–	–	<8.2	0.004±0.000	<0.01	–	–	–	Gallium
Germanium	<0.021	–	<260	–	–	–	0.013±0.004	<0.01	–	–	–	Germanium
Gold	–	–	< 0.0048	–	–	<0.0068	<0.009	–	–	–	–	Gold
Hafnium	–	–	< 0.074	–	–	0.0123±0.0010	0.017±0.001	–	–	–	–	Hafnium
Holmium	–	–	< 0.063	–	–	–	–	–	–	–	–	Holmium
Indium	–	–	< 0.1	–	–	<0.02	–	<0.01	–	–	–	Indium
Iodine	–	–	< 8.1	–	–	–	0.59±0.30	–	–	–	–	Iodine
Iridium	–	–	< 0.00037	–	–	<0.00006	<0.013	–	–	–	–	Iridium
Iron	1.01±0.28	–	<23	–	0.60±0.2	1.1±0.7	1.1±0.3	1.5±0.2	–	1.1[C], 1.45±0.19[D], 1.2[G], 1.5[H]	–	Iron
Lanthanum	–	–	< 0.3	–	–	<0.17	0.006±0.001	<0.01		–	–	Lanthanium
Lead	<0.075	–	<18000	–	–	–	0.0045±0.0007	0.02	–	<0.2[G]	–	Lead
Lithium	–	–	–	–	–	–	–	0.8±0.1		0.18±0.01[D]	–	Lithium
Lutetium		–	< 0.0059	–	–	<0.006	<0.002	–		–	–	Lutetium
Magnesium	–	–	<550	–	–	–	–	–	19.9±1.6	f	28.6[J]	Magnesium
Manganese	0.05±0.03	–	< 0.86	0.058	–	<0.23	0.12±0.04	0.12±0.01	<0.25	<0.1[G]	–	Manganese
Mercury	<0.045	–	< 0.14	–	–	<0.13	–	–	–	g	–	Mercury
Molybdenum	–	0.61±0.03	< 3.5	0.58	–	0.68±0.15	2.3±0.8	0.50±0.05	0.63±0.03		–	Molybdenum
Neodymium	–	–	< 0.29	–	–	<0.08	<0.003	–		–	–	Neodymium
Nickel	0.05±0.03		< 7	–	–	0.06±0.02	0.03±0.01	<0.01	<0.01	<0.1[G], 0.08[H]	–	Nickel
Niobium	–	–	<130	–	–	–	0.002±0.000	–		–	–	Niobium
Osmium	–	–	< 0.017	–	–	–	<0.02	–		–	–	Osmium
Palladium	–	–	< 9.2	–	–	–	<0.017	–		–	–	Palladium
Phosphorus	–	–	<2300	–	–	–	6.7±0.6	–	2.81±0.26	–	3.0[C], 0.28[F]	Phosphorus
Platinum	–	–	< 0.49	–	–	–	<0.025			–	–	Platinum
Potassium	–	–	<1500	–	–	<700	–	–		h	56[I]	Potassium
Praseodymium		–	<170		–	–	0.0020±0.0014				–	Praseodymium
Rhenium		–	< 0.024	–							–	Rhenium
Rhodium		–	< 3.7	–	–	–	<0.005				–	Rhodium
Rubidium	0.21±0.02	0.11±0.02	< 1.4	–		0.16±0.02	0.17±0.00	0.04±0.04		–	–	Rubidium
Ruthenium	–	–	< 0.52	–	–	–	<0.014			–	–	Ruthenium
Samarium		–	< 0.12	–	–	<0.0013	<0.004				–	Samarium

Table 4. CONTINUED

Element	Instrumental Methods[a]											Element
	X-ray Fluorescence Spectrometry		Instrumental Neutron Activation Analysis				Spark Source Mass Spectrometry	Emission Spectroscopy		Atomic Absorption Spectroscopy	Chemical and other Methods[a]	
								Optical	DC Plasma			
	A	D	B	C	D	A	E	F	D			
Scandium	–	–	0.00145±0.00036	–	0.0011±2%	0.0010±0.0003	<0.01	<0.01	–	–	–	Scandium
Selenium	0.18±0.01	0.18±0.03	0.38±0.08	–	0.17±0.04	0.25±0.03	0.094±0.000	–	–	–	–	Selenium
Silicon	–	–	<3900	–	–	–	18±4	–	9.2±0.4	9.8[C], 5.1±0.7[D], 4.0[F]	2.0[I]	Silicon
Silver	–	–	< 0.28	–	–	0.0044±0.0014	0.0025±0.0001	<0.01	–	0.0029±0.0005[A]	<0.1[G] –	Silver
Sodium	–	–	4210±840	4550	4503±24	4530±130	–	–	–	[j]	4500[I], 3685±212[J]	Sodium
Strontium	1.12±0.05	–	<24	–	1.03±0.07	<16	1.6±0.1	0.72±0.07	–	–	–	Strontium
Sulfur	–	–	<27000	–	–	–	–	–	–	–	2340[C], 989±14[E], 2700[H]	Sulfur
Tantalum	–	–	< 0.013	–	–	<0.0003	0.045±0.025	–	–	–	–	Tantalum
Tellurium	–	–	< 1.5	–	–	–	0.001	–	–		–	Tellurium
Terbium	–	–	< 0.0065	–	–	<0.0009	–				–	Terbium
Thallium	–	–	<450	–	–	–	<0.002	<0.01			–	Thallium
Thorium	<0.063	–	< 0.024	–	–	0.0037±0.0003	<0.006	–	–	–	–	Thorium
Thulium	–	–	< 0.013	–	–	–		–	–	–	–	Thulium
Tin	–	–	< 5.3	–	–	–	0.001	<0.01	–	10[H]	–	Tin
Titanium	0.14±0.10	–	<71	–	–	<43	1.3±0.0	0.03±0.003	<0.02	2[H]	–	Titanium
Tungsten	–	–	<0.62	–	–	<0.15	0.010±0.000	–	–	–	–	Tungsten
Uranium	0.59±0.03	–	< 0.91	0.51	0.52±0.07	0.41±0.02	1.08±0.18	–	–	–	0.65[G]	Uranium
Vanadium	0.11±0.08	–	< 0.89	–	–	<5	0.068±0.000	0.04±0.004	0.13±0.01	–	–	Vanadium
Ytterbium	–	–	< 0.025	–	–	<0.002	<0.005	<0.01	–	–	–	Ytterbium
Yttrium	<0.05	–	<2800	–	–	–	0.001±0.000	<0.01	–	–	–	Yttrium
Zinc	0.33±0.04	0.30±0.11	< 3	–	0.33±0.01	0.26±0.06	0.7±0.4	–	0.34±0.02	[k]	–	Zinc
Zirconium	0.49±0.27	0.88±0.03	<2000	–	–	–	1.0±0.0	0.51±0.05		–	–	Zirconium

[a]Superscript letters A through N are coded descriptors for the laboratories making measurements.

[b]Ba measurement made on a different x-ray system by measuring the Ba Kα x-rays induced in the sample prepared by laboratory A for NAA analysis with the 60 KeV gamma ray of ^{241}Am.

[c]8.0[C], 17±2[D], 6.45±0.07[E], 19[F], 14[G], 10.8[H], 12[I], 12.1[N]

[d]3900[C], 2530±127[E], 950[F], 1685±505[H], 4100±285[I], 3677±55[J], 822[N]

[e]56[C], 53[D], 68±0[E], 77[F], 60[G], 56[I], 50[N]

[f]12[C], 22.2±0.3[D], 26.5±0.7[E], 20[G], 10.4[H], 19[I], 19.3[N]

[g]0.021±0.003[A], <0.0002[E], <0.02[F], 0.0003[G], 0.0016[N]

[h]43[C], 51±0[E], 37[F], 56[G], 34[H], 53[N]

[i]0.07[C], 0.12[F], 0.25[G], 0.4[H]

[j]4290±114[B], 4100[C], 4402±32[E], 4400[F], 4400[G], 613[H], 4430[N]

[k]0.33±0.03[D], 0.24[F], 0.3[G], 0.37[H]

Table 5. ANALYSIS OF OMEGA-9 FOR WATER QUALITY PARAMETERS (mg/ℓ)

Parameter	Laboratory[a] (A)	(C)	(F)	(G)	(H)	(I)	(J)	(N)	Other
Alkalinity	16,600 ± 520	–	15,600	–	–	–	16,100 ± 344	16,600	–
Biochemical Oxygen Demand, 5-day	–	–	740	–	–	–	–	–	–
Carbon, Bicarbonate (as HCO_3^-)	–	15,100	15,300	–	13,255 ± 920	16,000	–	–	–
, Carbonate (as $CO_3^=$)	–	2100	660	–	3020 ± 780	0	–	–	–
, Inorganic (as C)	3690 ± 86	3400	–	–	2917 ± 231	–	–	–	–
, Organic (as C)	1130 ± 160	920	–	–	780	–	–	1300	1035 ± 104[K], 851 ± 18[M]
Chemical Oxygen Demand	5052 ± 83	–	7700	–	–	18,000	5679 ± 481	4154	–
Conductivity (μmhos/cm)	24,800 ± 1100	–	–	18,200	–	18,100 ± 850	–	–	–
Cyanide (as CN^-)	–	0.90	0.42	–	–	–	–	2.9	–
Hardness, Total (as $CaCO_3$)	–	–	–	–	62 ± 6	110	–	–	–
Nitrogen, Ammonia (as NH_3)	4070 ± 90	–	–	–	3218 ± 0	–	3846 ± 95	3643	4198 ± 680[J]
, Ammonium (as NH_4^+)	3290 ± 75	4890	–	–	2321	3400 ± 140	3300 ± 80	–	3600 ± 585[J]
, Kjeldahl (as N)	–	4000	3400	–	3280 ± 164	3000	–	–	–
, Nitrate (as NO_3^-)	–	–	0.17	–	–	–	–	–	–
, Organic (as N)	–	–	–	–	630	–	148 ± 28	–	–
Oil and Grease	–	580	–	–	–	–	–	–	–
pH	8.82 ± 0.03	8.5	8.6	8.5	9.0 ± 0.1	8.2	8.7	8.9	–
Phenols	56 ± 2	59	110	–	–	–	29.4	45	–
Phosphorus, Orthophosphate (as $PO_4^{\equiv}$)	–	6.7	0.08	–	–	–	24.6	–	–
Solids, Fixed	13,721 ± 10	–	–	–	–	–	13,135 ± 50	–	–
Solids, Total	–	–	–	14,200	14,340 ± 40	–	14,100 ± 494	–	–
Solids, Total Dissolved	–	–	13,900	14,200	14,340 ± 40	14,400	–	14,200	–
Sulfur, Sulfate (as $SO_4^=$)	2020 ± 160	2040	1200	1890	2500	1900	1710 ± 80	1875	–
, Sulfide (as S)	116 ± 12	0.0	–	–	–	–	–	176	–
, Sulfite (as S)	–	–	925	–	–	–	–	–	–
, Tetrathionate (as $S_4O_6^=$)	–	280	–	–	–	–	–	–	–
, Thiocyanate (as SCN^-)	110 ± 2	136	–	–	–	–	–	–	–
, Thiosulfate (as $S_2O_3^=$)	–	2225	–	–	–	–	3260	–	–

[a]Letters A–N are coded descriptors for laboratories making the measurements.

Table 6. CHARACTERIZATION OF OMEGA-9 TRUE IN-SITU SHALE PROCESS WATER (mg/ℓ)

Element	Total[a] Number of Measurements	Included in Best Value: Number[a] of Measurements	Number of Labs	Number of Techniques	Best Value[b] (mg/ℓ)	Coefficient of Variation
ELEMENTAL ANALYSES						
Aluminum	6	6	6	6	<0.03 - 19.1	
Antimony	7	7	6	4	1.9 ± 0.5	28%
Arsenic	12	12	7	6	1.0 ± 0.2	22%
Barium	7	5	4	3	0.71 ± 0.33	47%
Beryllium	2	1	1	1	<0.006	
Bismuth	2	1	1	1	<0.01	
Boron	6	6	6	4	27 ± 7	26%
Bromine	6	6	4	3	2.4 ± .4	18%
Cadmium	6	2	2	2	0.0016 ± 0.0008	53%
Calcium	14	12	10	4	12 ± 4	35%
Cerium	2	1	1	1	<0.026	
Cesium	4	1	1	1	(0.0021 ± 0.0003)[c]	
Chlorine	11	5	5	2	824 ± 61[d]	7.4%
Chromium	6	2	2	2	0.02 ± 4%	3.6%
Cobalt	8	5	5	3	0.030 ± 0.012	40%
Copper	10	7	4	3	0.10 ± 0.04	44%
Dysprosium	3	1	1	1	<0.006	
Europium	3	1	1	1	<0.0013	
Fluorine	8	7	7	3	60 ± 9	16%
Gallium	5	1	1	1	(0.004 ± 0.000)	
Germanium	4	1	1	1	(0.013 ± 0.004)	
Gold	3	1	1	1	<0.005	
Hafnium	3	2	2	2	0.015 ± 0.003	23%
Holmium	1	1	1	1	<0.063	
Indium	3	1	1	1	<0.01	
Iodine	2	1	1	1	(0.59 ± 0.30)	
Iridium	3	1	1	1	<0.00006	
Iron	10	9	6	5	1.2 ± 0.3	25%
Lanthanum	4	1	1	1	(0.006 ± 0.001)	
Lead	5	2	2	2	0.0045 - 0.02	
Lithium	2	2	2	2	0.18 - 0.8	
Lutecium	3	1	1	1	<0.006	
Magnesium	10	9	8	3	20 ± 6	30%
Manganese	8	4	4	4	0.09 ± 0.04	44%
Mercury	8	4	4	1	0.0003 - 0.021	
Molybedenum	7	5	5	4	0.60 ± 0.07	11%
Neodymium	3	1	1	1	<0.009	
Nickel	8	4	3	4	0.06 ± 0.02	38%
Niobium	2	1	1	1	(0.002 ± 0.000)	
Osmium	2	1	1	1	<0.06	
Palladium	2	1	1	1	<0.05	
Phosphorus	5	4	4	3	3.2 ± 2.6	83%
Platinum	2	1	1	1	<0.08	
Potassium	9	7	7	2	47 ± 9	19%
Praseodymium	2	1	1	1	(0.0020 ± 0.0014)	
Rhenium	1	1	1	1	<0.024	
Rhodium	2	1	1	1	<0.015	
Rubidium	6	4	2	3	0.16 ± 0.04	25%
Ruthenium	2	1	1	1	<0.042	
Samarium	3	1	1	1	<0.0013	
Scandium	5	3	3	1	0.0012 ± 0.0002	20%
Selenium	10	10	8	3	0.21 ± 0.11	53%
Silicon	7	6	5	4	8 ± 6	72%
Silver	6	3	2	3	0.003 ± 0.001	31%
Sodium	13	12	11	3	4333 ± 244	5.6%
Strontium	6	4	4	4	1.12 ± 0.36	33%
Sulfur	4	3	3	2	2010 ± 900	45%
Tantalum	3	1	1	1	(0.045 ± 0.025)	
Tellurium	2	1	1	1	(0.001)	
Terbium	2	1	1	1	<0.0009	
Thallium	3	1	1	1	<0.006	
Thulium	1	1	1	1	<0.013	
Thorium	4	1	1	1	(0.0037 ± 0.0003)	
Tin	4	4	4	4	0.001 - 10	
Titanium	7	7	6	6	<0.02-2	

Table 6. CONTINUED

Element	Total[a] Number of Measurements	Included in Best Value: Number[a] of Measurements	Number of Labs	Number of Techniques	Best Value[b] (mg/ℓ)	Coefficient of Variation
Tungsten	3	1	1	1	(0.010 ± 0.000)	
Uranium	7	5	4	3	0.55 ± 0.07	13%
Vanadium	6	2	2	2	0.12 ± 0.01	12%
Ytterbium	4	1	1	1	<0.002	
Yttrium	4	1	1	1	(0.001 ± 0.000)	
Zinc	11	9	5	5	0.31 ± 0.04	13%
Zirconium	5	4	3	4	0.73 ± 0.25	35%
WATER QUALITY PARAMETERS						
Alkalinity (as $CaCO_3$)	4	4	4	1	16,200 ± 480	3.0%
Biochemical Oxygen Demand, 5-day	1	1	1	1	(740)	
Carbon, Bicarbonate (as HCO_3^-)	4	0	0	0	(15,940)[e]	
Carbon, Carbonate (as $CO_3^=$)	4	0	0	0	(500)[e]	
Carbon, Inorganic (as C)	3	3	3	2	3340 ± 390	12%
Carbon, Organic (as C)	6	6	4	3	1003 ± 192	
Chemical Oxygen Demand	5	4	4	1	8100 ± 5700	70%
Conductivity (μmhos/cm)	3	3	3	1	20,400 ± 3840	19%
Cyanide (as CN^-)	2	2	2	2	0.42 - 2.9	
Hardness, Total (as $CaCO_3$)	2	1	1	1	(110)[f]	
Nitrogen, Ammonia[g] (as NH_3)	5	5	5	3	3795 ± 390	10%
Nitrogen, Ammonium (as NH_4^+)	6	6	5	3	3470 ± 830	24%
Nitrogen, Kjeldahl (as N)	4	4	4	2	3420 ± 420	12%
Nitrogen, Nitrate (as NO_3^-)	1	1	1	1	(0.17)	
Nitrogen, Organic (as N)	2	2	2	2	148 - 630	
Oil and Grease	1	1	1	1	(580)	
pH	8	8	8	1	8.65 ± 0.26	3.0%
Phenols	5	5	5	1	60 ± 30	51%
Phosphorus, Orthophosphate (as $PO_4^=$)	3	3	3	3	0.08 - 24.6	
Solids, Fixed	2	2	2	1	13,430 ± 415	3.1%
Solids, Total	3	3	3	1	14,210 ± 120	0.85%
Solids, Total Dissolved	5	5	5	1	14,210 ± 193	1.4%
Sulfur, Sulfate (as $SO_4^=$)	8	7	5	3	1990 ± 250	13%
Sulfur, Sulfide (as S)	3	1	1	1	(0.0)[h]	
Sulfur, Sulfite (as S)	1	0	0	0	<20[i]	
Sulfur, Tetrathionate (as $S_4O_6^=$)	1	1	1	1	(280)	
Sulfur, Thiosulfate (as $S_2O_3^=$)	2	2	2	2	2740 ± 730	27%
Sulfur, Thiocyanate (as SCN^-)	2	2	2	1	123 ± 18	15%

[a] The first column is the total number of measurements including upper and lower limits. The second column is the number of measurements used to compute the best value.

[b] The following rules were used to determine best values: (1) The smallest upper limit is reported unless that upper limit is for SSMS. In that case, the SSMS upper limit is multiplied by 3. (2) A range is reported if the coefficient of variation is greater than 100%. (3) Best values based on a single measurement are enclosed in parentheses. (4) Best values based on 2 or more measurements are determined using Dixon's procedure (32) following exclusion of values resulting from analytical errors. The reported error is 1 standard deviation if the number of measurements is greater than 1. Otherwise, it is the error reported by the laboratory making the measurements.

[c] The NAA value was selected based on conversations with the individual analysts.

[d] The measurements made using the Technicon Autoanalyzer and the mercuric nitrate methods were excluded due to interferences.

[e] Calculated using methodology shown in Table 8 and for C_T = 3336 mg/ℓ, pH = 8.6.

[f] Total hardness is the sum of polyvalent cations reported as $CaCO_3$. The reported value is consistent with value computed from Ca and Mg analyses reported in Table 6.

[g] This is the sum of NH_3 and NH_4^+.

[h] The presence of a very low sulfide level was verified by laboratories A and C using the qualitative AgS precipitation test.[39]

[i] The method used to measure sulfite has strong interferences. Based on qualitative analyses made by laboratory C, the sulfite level is <20 mg/ℓ. (Ref. 39).

of variation was 100%. If only upper limits were reported, the smallest upper limit was chosen except when SSMS was the analytical method. In that case, the reported upper limit was multiplied by 3 to account for a maximum factor of 3 variability noted for that technique in this study. When there were only two measurements, and when they diverged, the choice between them was based on conversations with the individual analysts. Those cases are documented in the footnotes to Table 6. Best values based on single measurements are enclosed in parentheses; these values are uncertain and require additional analysis for validation.

The use of this procedure with the elemental data (Table 4) resulted in the rejection of seven measurements as outliers and of six others due to chemical interferences. For the water quality parameters (Table 5), one measurement was rejected as an outlier and ten were rejected due to chemical interferences. Ranges were reported for six elements and three water quality parameters.

Elemental Characterization

The best values in Table 6 indicate that of the 72 elements measured in Omega-9 water (1) 32 were detected by two or more laboratories or techniques and fair agreement was obtained; (2) a range was reported for six elements; (3) 22 were below the detection limit of all techniques used; and (4) only a single measurement was used for an additional 12 elements.

The coefficient of variation reported in the last column of Table 6 demonstrates the agreement obtained among different laboratories and techniques. The average coefficient of variation for the 32 elements measured was 30%. Of those 32, the coefficient of variation was $\leqslant$ 10% for 3 elements (Cl, Cr, Na); 10% - <20% for 7 elements (Br, F, Mo, K, U, Zn, K); 20% -<30% for 7 elements (Sb, As, B, Hf, Fe, Rb, Sc); and $\geqslant$30% for 15 elements (Ba, Cd, Ca, Co, Cu, Mg, Mn, Ni, P, Se, Si, Ag, Sr, S, Zr).

Although the 30% average coefficient of variation obtained in this study is large compared with that obtained in some intercomparison studies using other sample types,[34] the results are encouraging. The present sample is highly contaminated, chemically complex, and the concentration of many measured constituents is close to the detection limit of applied techniques. The average concentration for 29 elements measured by two or more techniques is 6.3 mg/l. Additionally, other intercomparisons have focused on a single instrumental method.[34] This study employed six separate analytical techniques for which a wide range of sample preparation methods was used. Thus, the sources of variability include not only instrumental error and sample handling, but uncertainties due to different sample preparation methods.

A range was reported for Al, Li, Pb, Hg, Sn, and Ti. The large variations for these elements are probably due to interferences or to sample handling and preparation methods. Since all of these elements

are environmentally important, work should be directed at discovering the source of the variability and correcting it.

Water Quality Parameters

The best values in Table 6 indicate that of the 28 water quality parameters measured in Omega-9 water, 16 were detected by two or more laboratories and fair agreement obtained; a range was reported for 3; 1 was below the detection limit; and 8 were measured by only a single laboratory.

Quantitative data based on two or more measurements were obtained for alkalinity, organic and inorganic C, conductivity, NH_3, NH_4^+, Kjeldahl N, pH, phenols, solids, $SO_4^=$, $S_2O_3^=$, SCN^-, and COD. The coefficient of variation reported in the last column of Table 6 demonstrates the agreement obtained among different laboratories and techniques. The average coefficient of variation for the 16 parameters is 18%, significantly better than the 30% coefficient obtained for the elemental analyses. However, in general, the accuracy obtained for the water quality parameters is poorer than that for the elements. (This will be discussed in the section on "Analytical Considerations.") Of these 16 parameters, the coefficient of variation was <5% for 5 parameters (alkalinity, pH, solids); 5% - <20% for 7 parameters (inorganic and organic C, conductivity, NH_3, Kjeldahl N, $SO_4^=$, SCN^-); and ≥20% for 4 parameters (COD, NH_4^+, phenols, $S_2O_3^=$). However, the average concentration of 13 water quality parameters measured by two or more laboratories (pH, phenols, SCN^- excluded) is 8,200 mg/l, which is 1,300 times higher than that of the average concentration for 29 elements (6.3 mg/l).

The results obtained for CN^-, organic N, and $PO_4^{\equiv}$ varied widely and only a range is reported in Table 6. Coefficients of variation greater than 50% were obtained for phenols and COD. The variability in these parameters is probably due to significant interferences and/or stability problems.

Relative Instrumental Performance

An approximate criterion of performance for each laboratory and instrumental technique is summarized in Table 7. Table 7 presents the mean, standard deviation, coefficient of variation, and uncertainty in the coefficient of variation for normalized measurements. Normalized measurements were computed by dividing each value in Tables 4 and 5 by the best value from Table 6. Only elements or waters quality parameters detected by two or more laboratories or techniques for which a coefficient of variation is reported in Table 7 are included in the normalized measurements. The coefficient of variation is a measure of accuracy for the elemental analyses; the normalized mean, if significantly different from 1, indicates systematic errors of measurement. Performance increases as the normalized mean approaches 1 and as the coefficient of variation decreases.

Table 7. LABORATORY AND TECHNIQUE PERFORMANCE EXPRESSED AS A NORMALIZED AVERAGE AND COEFFICIENT OF VARIATION

Elemental Analyses[a]	Number of Elements Included in Normalized Average (N)	Normalized Average ($\bar{X} \pm 1\sigma$)	Coefficient of Variation $\left[\frac{1\sigma}{\bar{X}}\right]100$	Uncertainty in Coefficient of Variation $\frac{\left[\frac{1\sigma}{\bar{X}}\right]100}{\sqrt{2(N-1)}}$
X-ray Fluorescence (A)	14	0.96 ± 0.21	22%	4%
X-ray Fluorescence (D)	9	1.02 ± 0.31	30%	8%
Neutron Activation Analysis (A)	16	0.97 ± 0.22	23%	4%
Neutron Activation Analysis (B)	7	1.09 ± 0.35	32%	9%
Neutron Activation Analysis (C)	10	0.94 ± 0.17	18%	4%
Neutron Activation Analysis (D)	12	0.94 ± 0.20	21%	5%
Spark Source Mass Spectrometry (E)	23	1.29 ± 0.78	60%	9%
Optical Emission (F)	12	1.14 ± 0.60	53%	11%
D.C. Plasma Emission (D)	11	0.88 ± 0.25	28%	6%
Atomic Absorption Spectroscopy	13	1.03 ± 0.17	17%	3%
Other	12	1.15 ± 0.80	70%	15%
Water Quality Parameters[a]				
Laboratory A	12	1.00 ± 0.15	15%	3%
Laboratory C	9	1.05 ± 0.17	16%	4%
Laboratory F	7	1.05 ± 0.39	37%	11%
Laboratory G	5	0.96 ± 0.05	5.2%	2%
Laboratory H	10	0.90 ± 0.20	22%	5%
Laboratory I	8	1.11 ± 0.44	40%	11%
Laboratory J	10	0.92 ± 0.19	21%	5%
Laboratory N	8	0.94 ± 0.23	24%	6%

[a]Letters A - N are coded descriptors for laboratories making measurements.

Because of the uncertainties in the true value of the abundances of an element when determined by averaging the results of different laboratories, there is an uncertainty in the coefficient of variation. This uncertainty is reported in the last column of Table 7. Therefore, small differences may not be significant. Of the 11 laboratories/techniques used for elemental analyses, 8 have coefficients of variation between 15% and 30% and three have a coefficient of variation between 50% and 70%. There is no statistically significant difference in the performance within each of these groups, but there is between the groups. Thus, the performance of XRF, NAA, PES, and AAS in this study was significantly better than that of SSMS, OES, and other methods. Similarly, of the eight laboratories reporting water quality analyses, five have coefficients of variation between 15% and 25% and two have coefficients of variation between 35% and 40%. The coefficient of variation for the eighth laboratory, G, falls into a group of 1. Thus, there was a statistically significant difference in performance for analysis of water quality parameters.

The NAA, XRF, and AAS results are the most consistent and accurate of the instrumental techniques evaluated. OES, PES, and SSMS have normalized means significantly different from 1, suggesting systematic errors. However, SSMS detected more elements than any other technique evaluated and consistently had the lowest detection limit. The "other" techniques shown in Table 7 include specific ion electrode and colorimetric and wet chemical measurements. The deviant mean and high coefficients of variation for these measurements are due primarily to chemical interferences encountered with the chlorine measurements.

ANALYTICAL CONSIDERATIONS

Many of the analytical techniques investigated in this study are inadequate for the analysis of complex matrices such as oil-shale process waters. Standard analytical methods including Standard Methods,[11] EPA's methods,[12] ASTM methods,[25] and USGS methods[14] are often not applicable to these types of waters due to interferences and to the extremely high or low levels of many parameters. Each method should be evaluated on a case-by-case basis when used for highly complex samples. Nevertheless, most participating laboratories used these methods without modification. This points to the urgent need to develop and publish methods specific to complex sample types not heretofore widely analyzed.

Although many of the wet chemical techniques evaluated gave reproducible results, the accuracy of measurement was poor due to interferences. This is true for Cl^-, $S^=$, $SO_3^=$, solids, and $CO_3^=$.

The primary interferences for wet chemical measurements are high concentrations of organic or inorganic S, C, and N compounds; the presence of strong color and emulsified oil and grease; and the diversity of organic compounds. Some C, N, and S compounds combine with analytical reagents, producing erroneous results. This type of interference affects the measurement of COD, $S^=$, $SO_3^=$, and Cl^-. The presence of color and oil and grease interfere with some colorimetric and electrode measurements. This type of interference may affect both the precision and accuracy of

measurement of F^-, conductivity, pH, alkalinity, $CO_3^=$, $HCO_3^=$, $PO_4^=$, phenols, and Cl^-.

The precision obtained for many of the water quality parameters using the same method in different laboratories was poor and generally outside of quoted precisions.[11,12] This is true for COD, phenol, inorganic and organic C, conductivity, NH_3, $SO_4^=$, $S^=$, and $SO_3^=$. The poor precision is probably due to differences in pretreatment selected by the individual laboratories to mitigate suspect interferences, and to the presence of color, oil, and grease, all of which interfere with colorimetric and electrode methods.

The determination of HCO_3^-, $CO_3^=$, NH_3, NH_4^+, $S^=$, H_2S, and other species may depend on equilibrium calculations. The ionic strengths of Omega-9 and of similar waters, however, is so high ($I \geqq 0.5$) that the usual assumption of infinite dilution is not valid. Approximations, such as the Debye-Huckel or Davies, to correct equilibrium constants for ionic strength are invalid for $I > 0.5$ (Ref.35). Laboratory measurements of appropriate equilibrium constants need to be made so these species can be accurately determined.

Fewer interferences were identified for the instrumental methods (NAA, XRF, SSMS, AAS, OES, PES) than for the chemical methods of analysis. The extremely high Na level in the sample limited the sensitivity of NAA measurements where radiochemical separation was not used and interfered with some AAS, OES, and PES measurements. However, the overall precision of measurement was poorer than for the chemical methods. A major reason for this is that the mean concentration of elements determined instrumentally was 6.3 mg/l; it was 8,200 mg/l for the water quality parameters. Another factor is the variety of sample preparation methods used. There are few standard methods for instrumental analysis, except AAS.

A number of the more significant interference problems noted in this study are summarized and discussed below; other interferences are summarized in Table 3. The discussion is limited to those constituents that occur at high levels in Omega-9 or to those with interferences that are understood by the authors. Additionally, routine chemical methods that appear to be suitable for analysis of waters like Omega-9 are identified.

Chlorine

A significant analytical problem attends the measurement of Cl in oil-shale process water. The four methods used to measure Cl--NAA, XRF, $Hg(NO_3)_2$ titration, and the Technicon AutoAnalyzer--produced highly variable results. Although NAA and XRF measure total Cl and the chemical methods measure Cl^-, this distinction cannot account for the large variability apparent in Table 4.

The Cl data have a trimodal distribution. The results obtained by NAA and the single XRF measurement average 824 ± 61 mg/l; by the Technicon AutoAnalyzer, 4,000 ± 140 mg/l; and by the $Hg(NO_3)_2$ titration method, 2,211 ± 1,171 mg/l. The NAA and Technicon AutoAnalyzer results are consistent within each method while the $Hg(NO_3)_2$ results show large dispersion.

The Technicon AutoAnalyzer and the $Hg(NO_3)_2$ method both have interference problems that were not considered in running the tests; those problems are discussed below. Therefore, these results have not been used to compute the best value for Cl in Table 6. In contrast, there is no known interference for Cl measured by NAA or XRF methods used in this work. Consequently, the NAA and XRF measurements were used to compute the Cl value shown in Table 6.

The high values and dispersion obtained with the chemical methods can be explained by examining the analytical methods in more detail. The $Hg(NO_3)_2$ method is recommended in Standard Methods[11] and by the EPA[12] for the analysis of Cl^- in waters. It consists of titrating an acidified sample with $Hg(NO_3)_2$ using diphenylcarbazone as the endpoint indicator. Tests with this method in one of the author's laboratories indicate that there is an interference problem.

The method is based on the reaction:

$$2Cl^- + Hg^{+2} \leftrightharpoons HgCl_2\ (aq) \qquad (1)$$

However, in the presence of other constituents that react with Hg, the method gives results that are high.

A number of constituents present in Omega-9 may form precipitates with the Hg used for titration. These include SCN^-, $SO_4^{=}$, $S_2O_3^{=}$, and some carboxylic acids. During titration, a gelatinous precipitate forms before the endpoint is reached. Its formation has two effects: first, the endpoint is postponed, which causes a high result; and second, the muddy precipitate makes detection of the endpoint difficult. This latter point probably accounts for the dispersion in the $Hg(NO_3)_2$ titration results. An additional minor interference is the simultaneous titration of Br^- and I^-.

Oxidation with $KMnO_4$ removes the interference for some waters, yielding results equivalent to those obtained by instrumental analysis. In the $KMnO_4$ method developed at the laboratory of one author, the sample is diluted 1:10 with distilled water, acidified to pH < 1 with HNO_3, heated to boiling, cooled in a water bath, 5 ml 0.2 N $KMnO_4$ added, and the sample titrated with 0.141 N $Hg(NO_3)_2$. Additional work is required to standardize the method and extend it to a wider range of oil-shale process waters.

The Technicon AutoAnalyzer uses a colorimetric method[12] in which SCN^- is liberated from $Hg(SCN)_2$ when Hg reacts with Cl^- to form $HgCl_2$. In the presence of ferric ion, SCN^- forms the highly colored ferric thiocyanate in proportion to the original Cl^- concentration. The presence

of SCN^- and color interfere with this method. Additionally, Hg reacts with constituents other than Cl^-, analogous to the $Hg(NO_3)_2$ titration interference, yielding high results.

Sulfide

Sulfide is measured quantitatively by the methylene blue or iodine titrimetric methods[11,12,26] and qualitatively by the lead acetate paper, antimony, or silver foil tests.[11] In this work, the qualitative methods and the iodine titrimetric methods following a CO_2 purge into $Zn(C_2H_3O_2)_2$ or $CdSO_4$ were used. Table 5 indicates that there is considerable disagreement between these two methods. The titrimetric method yielded an average $S^=$ concentration of 146 mg/l-S and the qualitative test indicated that $S^=$ was absent.

The presence of reducing agents in oil-shale process waters interferes with the quantitative tests. Notable among these are $S_2O_3^=$ and various organics. The high (2,743 mg/l) $S_2O_3^=$ concentration in Omega-9 would prevent the formation of the blue color in the methylene blue method. If the sample is titrated directly, $S_2O_3^=$, phenol, and unsaturated fatty acids will react with I^-, yielding high results. If acidification and purging are used, reducing S compounds are decomposed, producing erratic results, or volatiles are purged along with the H_2S, which subsequently react with I^- during titration, again yielding high results.

Both Standard Methods[11] and EPA methods[12] recommend pretreatment to eliminate these interferences. Pretreatment consists of precipitating the $S^=$ as ZnS by adding 2 N $Zn(C_2H_3O_2)_2$ followed by separation of the precipitate. This pretreatment was not used in this study as the presence of high levels of reducing agents was not suspected. Therefore, results reported using the titrimetric method are in error and are not used to compute the best value for $S^=$ summarized in Table 6.

The qualitative tests, on the other hand, are relatively free of interferences. Results obtained by laboratory C and subsequently by the authors suggest that $S^=$, if present, occurs at low levels in Omega-9.

It is recommended that pretreatment be used if standard analytical methods are used for the measurement of $S^=$ in oil shale process waters. The $Zn(C_2H_3O_2)_2$ pretreatment procedure should be evaluated in the laboratory to determine if it is suitable for oil shale retort waters.

Organic Carbon

The data in Table 5 suggest that there is an analytical problem associated with the measurement of TOC in Omega-9. The reported TOC values range from 780 to 1,300 mg/l and average 1,003 ± 193 mg/l. These values were obtained using several commercially available instruments and both direct methods (inorganic C removed by acidifying and purging) and indirect methods (computed from independent measurements of total and inorganic C).

There are three principal sources of error in the standard TOC procedure when it is applied to oil shale process waters. These are: (1) the presence of suspended or emulsified organics and large organic particles that are not taken up in microsyringes; (2) the formation of precipitates when the sample is acidified; and (3) the loss of volatiles on purging with N_2 or on storage. The loss of volatiles and precipitate formation are eliminated when the indirect method is used.

Heterogeneities due to suspended materials, large organic particles, or precipitates may be minimized by using large sample size for analysis. If that is not possible, an effort to homogenize the sample should be made. Laboratory M noted that precipitation formation was alleviated by using dilute 1M HCl instead of concentrated HCl for acidification.

Volatile organic carbon was measured at 250 mg/l by laboratory M. Those volatiles could be lost during N_2 purging or during storage since the samples were not maintained under an N_2 blanket. A method to eliminate the loss of volatiles during the purging has been published[33] and should be investigated for application to oil shale process waters.

Chemical Oxygen Demand

The chemical oxygen demand (COD) of a water is a measure of the oxygen equivalent of the organic matter that is oxidized by a strong chemical oxidant. The parameter is conventionally used to assess the performance of biological treatment processes and to estimate the effect of waste discharges on the oxygen level in receiving waters; in addition, it is sometimes used to regulate the discharge of organic wastes. The COD is measured in terms of the amount of potassium dichromate ($K_2Cr_2O_7$) reduced by a sample during a 2-hr reflux in a solution of boiling, 50% H_2SO_4 and in the presence of a Ag_2SO_4 catalyst. $HgSO_4$ is added to complex Cl^- and thus prevent its oxidation to Cl_2. Essentially complete (theoretical) oxidation of many organic compounds is obtained in the presence of the catalyst. Straight-chain aliphatic compounds, aromatic compounds, and many N compounds are incompletely oxidized.[11,36]

The COD data summarized in Table 5 range from 4,154 to 18,000 mg/l, a range that is significantly outside of the precision of the method reported in Standard Methods.[11] The fact that in-laboratory precision is good while between-laboratory precision is poor suggests that the method is very sensitive to some part of the procedure that is not carefully controlled since all laboratories but one used the same method. The variability may be related to the fact that neither Standard Methods[11] nor the EPA methods[12] specify an upper limit for the COD concentration. The ASTM COD method,[36] which is procedurally identical to these two methods, specifies an upper limit of 800 mg/l COD for a 50-ml sample treated with 25 ml of 0.25 N $K_2Cr_2O_7$. The maximum COD that can be measured using a 50 ml sample and 25 ml of 0.25 N $K_2Cr_2O_7$ is 1,000 mg/l (Ref. 37). A sample with a COD greater than 1,000 mg/l, such as Omega-9, would therefore have to be diluted to bring it within the range for the method. Thus, different dilutions could cause the noted variability. The high Cl^- concentration could also contribute to the variability if

the Hg added to complex Cl^- were complexed by constituents other than Cl^-. Both the Standard Methods and EPA method for COD should be modified to include appropriate statements on the upper limits of the method.

Any inorganic compound that is oxidized by $K_2Cr_2O_7$ in an acid medium will contribute to the measured COD and give a high value. The principal known interferences from this source in Omega-9 are $S_2O_3^=$ and $S_4O_6^=$ (Refs. 38,39). For example, the $S_2O_3^=$ is readily oxidized by $K_2Cr_2O_7$ to $SO_4^=$ in acid media as follows:

$$4\ Cr_2O_7^= + 3\ S_2O_3^= + 26\ H^+ \longrightarrow 6\ SO_4^= + 8\ Cr^{+3} + 13\ H_2O \qquad (2)$$

Thus, for each milligram of $S_2O_3^=$ present in a sample, 0.285 ml of 0.25 N $K_2Cr_2O_7$ will be consumed, yielding a high result. The effect of this on the measured COD can be theoretically computed using Eq. (2). Since Omega-9 has an $S_2O_3^=$ concentration of 2740 mg/l, the theoretical COD due to oxidation of $S_2O_3^=$ to $SO_4^=$ is 1270 mg/l COD.

The standard COD test[11,12] should be modified to correct for the oxidation of inorganic S compounds before the test is applied to oil-shale process waters containing high levels of compounds. Experimental work is required to develop a method to eliminate this interference. Additionally, the ability of the recommended quantities of Ag_2SO_4 and $HgSO_4$ to, respectively, catalyze the oxidation of certain organics and complex Cl^-, should be verified experimentally for oil-shale process waters.

Solids

Total dissolved and fixed solids were measured with good precision; however, the significance of those measurements for waters similar to Omega-9 is questionable.

Total dissolved solids (TDS) as operationally defined in Standard Methods[11] and by EPA[12] is the residue remaining after a sample has been filtered and dried at 103°-105°C or at 180°C. This parameter is intended to be a good indicator of total dissolved salts, which are not significantly lost on heating. However, this parameter is a poor indicator of the dissolved salts in waters similar to Omega-9. This could be a significant problem if this parameter is used to make regulatory decisions or to design treatment facilities.

The degree by which the measured TDS differs from the total dissolved salts present in Omega-9 is indicated by the following. The average measured TDS for this water is 14,210 mg/l while the calculated total dissolved salts is 30,300 mg/l. The factor of 2 difference between the measured and calculated TDS is typical of the results obtained with these waters.

The species $CO_3^=$, HCO_3^-, NH_3, and NH_4^+ constitute over 65 weight percent of the dissolved salts present in Omega-9. On heating at 103°-105°C, these species are lost from solution through the formation of volatile salts or by stripping out dissolved gases. Linstedt, Daniel, and Bennett[38] investigated lyophilization and evaporation of Omega-9 at

room temperature, as an alternative to evaporation at 103°-105°C or 180°C, and found that neither procedure gave satisfactory results. Substantial losses of NH_4HCO_3 occurred even at freezing temperatures. Therefore, the TDS determination, irrespective of the drying temperatures, gives a value that is significantly low for oil-shale process waters and is not representative of the dissolved salts present.

The same considerations apply to total solids. Work needs to be directed at developing a method to measure both total solids and TDS in these types of waters that accurately reflects the level of salts present. This may be approached by determining a temperature at which a significant fraction of the ammonia and carbonate species is lost without loss of other components. The TDS could then be measured by running the standard analysis at this elevated temperature and adjusting the value obtained by adding to it NH_4^+, $CO_3^=$, and HCO_3^-. Alternatively, the CO_2 and NH_3 lost during the TDS test could be collected and determined gravimetrically.

Alkalinity, Biocarbonate, Carbonate

Conventionally,[11,12] HCO_3^- and $CO_3^=$ are determined from alkalinity and pH measurements. However, that method is not valid for oil-shale process waters due to the presence of buffering components other than the $CO_3^=$ system (ammonia, borate, silicate, organic bases) and the high ionic strength of the water. The presence of these species results in an overestimation of $CO_3^=$ when the Standard Method[11,12] is used.

Since all of the participating laboratories used conventional methods to determine HCO_3^- and $CO_3^=$ the measurements reported in Tables 4 and 5 were not used to determine the best values shown in Table 6. Instead, an alternative method was used to compute those species. This method is described below and is recommended for the measurement of HCO_3^- and $CO_3^=$ in any water not buffered exclusively by the $CO_3^=$ system.

An alternative way to determine HCO_3^- and $CO_3^=$ is to measure the total inorganic C and pH and to use equilibrium expressions to compute the distribution of HCO_3^- and $CO_3^=$. This method is discussed by Stumm and Morgan[35] and is summarized and applied to Omega-9 water in Table 8. Note that the equilibrium constants K_1 and K_2 must be adjusted for the ionic strength of the sample. Alternatively, a back titration may be used in conjunction with the usual strong acid titration.

The computed value for HCO_3^- compares favorably with the average of all analytical determinations in Table 4 (15,940 vs 14,900 mg/l). However, the $CO_3^=$ values are not in agreement (500 vs 1,720 mg/l). This is primarily due to the variation in measured pH and the presence of buffering components which are neutralized during titration above the $CO_3^=$ equivalence point. This is confirmed for Omega-9 by equivalence points at 7.5 and 4.3

Table 8. COMPUTATION OF HCO_3^- AND $CO_3^=$ FROM MEASUREMENTS OF INORGANIC C AND pH

Carbonate species distribution

$$[HCO_3^-] = \alpha_1 C_T$$

$$[CO_3^=] = \alpha_2 C_T$$

$$\alpha_1 = \left[\frac{[H^+]}{K_1} + \frac{K_2}{[H^+]} + 1\right]^{-1}$$

$$\alpha_2 = \left[\frac{[H^+]^2}{K_1 K_2} + \frac{[H^+]}{K_2} + 1\right]^{-1}$$

C_T = dissolved inorganic carbon, mg/ℓ as C

Ionic strength

$$I = 1/2 \sum_i C_i Z_i^2$$

Z_i = ionic charge

C_i = molar concentration

Adjustment of equilibrium constants

$$pK' = pK - AZ^2\left[\frac{\sqrt{I}}{1+\sqrt{I}} - 0.3I\right]$$

$A \simeq 0.5$

Application to Omega-9

I	=	0.5
pK_1	=	6.22 at 25°C
pK_2	=	9.80 at 25°C
α_1	=	0.94
α_2	=	0.06
C_T	=	3340 mg/ℓ
HCO_3^-	=	15,940 mg/ℓ as HCO_3^-
$CO_3^=$	=	500 mg/ℓ as $CO_3^=$
pH	=	8.65

Recommended Analytical Methods

Based on the results of this study and the authors' experience with analytical instrumentation, the following instrumental techniques are recommended for the analysis of waters similar to Omega-9.

Instrumental Methods -

XRF: As, Br, Ca, Cu, Fe, Ni, Rb, Se, Sr, Ti, U, V, Zn, Zr, Mo, Cl

NAA: Sb, As, Br, Cl, Co, Mn, Hf, Ce, Ba, Fe, Mo, Ni, Sm, Se, Na, Sr, U, Zn

AAS: Se, Ca, Fe, Na, Zn, Mg, K

Chemical and Other Methods -

The following chemical methods are recommended for analysis of oil-shale process waters pending further laboratory evaluation.

1. Arsenic: silver diethyldithiocarbamate[11]
2. Chloride: $KMnO_4$ oxidation/$Hg(NO_3)_2$ titration (this work)
3. Sodium: Technicon AutoAnalyzer
4. Uranium: Fluorimetric[31]
5. Fluoride: Specific ion electrode[11]
6. Sulfate: Gravimetric[11]
7. Thiocyanate: Colorimetric[11]
8. Total Sulfur: Gravimetric[30]
9. Inorganic Carbon: Carbon Analyzer[11]
10. Alkalinity: Titrimetric[11,12]
11. $HCO_3^-/CO_3^=$: Calculation from inorganic C and pH (Table 8)

These recommendations are based on collaborative results from several methods or from extensive knowledge of the technique. Emission techniques and SSMS are not recommended because the data base compiled in this study is not adequate to assess their general performance. Additionally, the performance of these techniques as measured by the normalized average and coefficient of variation (Table 7) was poor.

Elements other than those listed above may be determined by XRF, NAA, and AAS. The specific elements measured depend on the design of the instrumentation. A good example of this is XRF. Laboratories using XRF in this study used energy-dispersive systems and high energy X-rays (except laboratory N). Alternatively, a wavelength-dispersive system using low-energy X-rays could be employed and another set of elements, including Na, Ca, Fe, Si, Mg, and Cl, determined.

Based on the work presented here, the 11 chemical methods appear adequate for use with waters like Omega-9. However, the authors encourage additional collaborative work on these methods to establish their validity on a range of oil-shale process waters before any major analytical work is undertaken. The other chemical methods used in this study require modification to correct for interferences.

CHEMICAL SIGNIFICANCE OF OMEGA-9 WATER

The composition of this water is influenced by the intrusion of groundwater into the formation (see Ref. 3 for groundwater composition), process operating conditions, and oil shale composition. The water-to-oil ratio of 22 obtained during the acquisition of the Omega-9 sample[1] suggests that approximately 22 parts of groundwater were mixed with 1 part of combustion water plus dehydration water. The chemistry of this specific water is dominated by an alkaline pH and the presence of high levels of organic and inorganic C, N, and S as well as Na and Cl. The high level of organic and inorganic C, N, and S is typical of oil-shale process waters and the high level of Na and Cl are atypical of these waters and probably originated from groundwater intrusion.

The TDS, as determined from the sum of the individual ions, is about 30,300 mg/l, which is roughly equal to the TDS of seawater. The principal ions, present at levels greater than 1,000 mg/l, are Na^+, NH_4^+, HCO_3^-, $S_2O_3^{=}$, and $SO_4^{=}$; they constitute about 95% of the total salts present on a weight basis. Other constituents present at levels of 10 to 1,000 mg/l are B, Ca, Mg, K, $CO_3^{=}$, Cl^-, F^-, $S_4O_6^{=}$, and SCN^-. Constituents present at levels of from 1 to 10 mg/l are Sb, As, Br, Fe, P, Si, and Sr. Other constituents are present at levels below 1 mg/l.

A charge balance for Omega-9 water is presented in Table 9. This balance is based on the best values summarized in Table 6. The percent variation (1.9%) is considerably less than the recommended limit of 3%. The good agreement of the charge balance lends credibility to the accuracy of some of the analytical results determined in this study.

SUMMARY

This study has evaluated existing chemical and instrumental methods for the characterization of an oil-shale process water. It demonstrated that many standard analytical methods cannot be used to accurately measure water quality parameters in these complex waters. Methods specific to these waters need to be developed and published. The following methods were found to give incorrect results when used on waters like Omega-9:

Table 9. CHARGE BALANCE FOR OMEGA-9 WATER

CATIONS			ANIONS		
	mg/ℓ	meq/ℓ		mg/ℓ	meq/ℓ
Calcium	12	0.60	Bicarbonate	15,940	261.27
			Carbonate	500	16.66
Magnesium	20	1.65	Chloride	824	23.24
			Fluoride	60	3.16
Potassium	46	1.18	Sulfate	1990	41.44
			Thiosulfate	2740	48.93
Sodium	4333	188.47	Tetrathionate	280	2.50
			Thiocyanate	123	2.12
Ammonium	3470	192.71			
TOTAL		384.61			399.32

$$\% \text{ Variation} = \left[\frac{|x_1 - x_2|}{x_1 + x_2}\right] 100 = 1.9\%$$

(1) $Hg(NO_3)_2$ titration and Technicon AutoAnalyzer methods for Cl^-; (2) titrimetric method without pretreatment for $S^=$; (3) gravimetric method for solids; and (4) the permanganate oxidation method for COD. Other methods, including those for CN^-, phenols, $PO_4^{\equiv}$, and $CO_3^{=}$, do not yield reproducible results. There may be interferences in other methods used in this study but there are presently inadequate data to assess them. Some existing chemical methods for the measurement of alklalinity, $SO_4^{=}$, inorganic C, Na, SCN^-, As, and total S, and the methods presented in this work for $CO_3^{=}$, HCO_3^-, and Cl^- may be adequate for routine analyses following limited additional laboratory testing.

The instrumental methods used were found to be free of interferences, with the exception of the high Na concentration. Since this is not typical of oil-shale process waters, this may not be a problem for other oil-shale process waters. However, instrumental methods are subject to variations due to differences in sample preparation and the fact that most of these techniques produce precision data for a subset of the total set of elements reported. Results obtained with SSMS and the emission techniques were poor compared with those obtained with other instrumental methods. SSMS consistently gave the lowest detection limit but had the poorest precision of all instrumental methods evaluated. XRF, NAA, and AAS produced precise and accurate results.

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