

Characterisation of oilfield waters

What types of water?

Formation water, produced water, injection waters, surface waters, core waters, water associated with drilling mud etc.

What species are determined?

The most common suite of analytes is:

Anions: chloride, sulphate, bromide, total carbonate species expressed as bicarbonate, C₁- C₄ straight chain organic acid anions (formate, acetate, propionate and butyrate, often referred to as VFAs within the oil industry) and boron.

Cations: barium, strontium, calcium, magnesium, sodium, potassium, iron, copper, zinc, manganese, aluminium and lithium

Elements: sulphur, phosphorus, silicon.

On rare occasions other analytes used as tracers such as iodide, fluoride, thiosulphate and thiocyanate are determined, on other occasions dicarboxylic acid anions such as malonate and succinate are quantified as well as "nutrients" such as ammonium and nitrate. In addition to the ionic composition, pH is always determined where sample volume permits and other physical parameters such as resistivity, density, viscosity are often determined.

What techniques are used?

The normal suite of analyses requires a combination of at least four techniques, depending on the concentration of species present. Expro's analytical data services employ optimum analytical conditions and techniques for each species. Chloride is determined by either potentiometric titration or ion chromatography (IC), depending on the levels present. Sulphate is determined by IC using suppressed conductivity, bromide is determined by IC using UV detection. Total carbonate species expressed as bicarbonate and the C₁- C₄ acid anions are determined by ion exclusion chromatography (IEC) using suppressed conductivity. If no formate or acetate is present the carbonate species can be speciated by potentiometric titration. Cations and transition metals are determined by inductively coupled plasma (ICP) although for some species where lower detection limits are required atomic absorption (AA), IC or ICP-MS may be employed.

All analyses where external calibrations are employed (eg IC, IEC and titration) are carried out in duplicate. Where internal standards are used in addition to external calibrations (eg ICP) analysis is carried out once for each sample.

What are the limits of detection?

Limits of detection for each species may be affected by the presence of interfering species, the relative concentration of the species of interest and the sample mass provided. If there are no interference problems then for species determined by ion chromatography LOD's of 0.1 – 1.0 mg/kg for most species are usually attainable. For ion exclusion chromatography 1 mg/kg of each species may be detected, whilst for ICP single mg/kg detection limits are normal.

How are the results reported?

Data sets are routinely reported in wt/wt units (eg mg/kg) since dilutions carried out by weight are intrinsically more accurate than volumetric dilutions. In general the results are tabulated in an excel spreadsheet (as shown below) which is incorporated into a word document that includes additional information such as method summaries, uncertainty statements, ionic balances and data interpretation where appropriate. The customer receives electronic copies of the spreadsheet and final report (word document) and a hard copy of the final report. However Expro's analytical data services operates a flexible system for reporting results according to the customer's requirements, including sending regular updates as work is progressed.

How much sample is needed?

In general volumes of 100 – 200 mL are optimum as this affords easy sub sampling and multiple analyses where many dilutions are necessary, for example when concentrations of all the species of interest vary greatly. However Expro's analytical data services can provide a characterisation of water on as little as 100 μ L of sample (in the case of water samples spun from cores), although limits of quantification will be compromised to some extent since, in such cases, the need to dilute is based on sample volume availability rather than analyte concentration.

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Is there an optimum sampling protocol?

In general for stabilised samples the sample container should be chosen such that it can be filled to the top leaving no headspace. HDPE or Nalgene vessels are recommended since they can not break and the internal surfaces are much cleaner than those made of glass. Live samples should be sent in suitable pressurised vessels. For single liquid phase pressurised samples these should be transported in a vessel that incorporates a gas chamber for expansion.

Technical Specifications:				
Expro's analytical data services reference	EADS xxxxx	EADS xxxxx	EADS xxxxx	EADS xxxxx
Customer reference (i)	ABC	DEF	GHI	JKL
Customer reference (ii)	123	124	125	126
Physical Parameters				
pH @ 25C (pH units)	7.10	6.98	7.27	7.54
Anionic Species (mg/kg)				
Chloride	6195	12456	18765	34258
Sulphate	24	48	71	342
Bromide	6.1	43.3	263	321
Bicarbonate	95	190	285	785
Formate	12	25	37	62
Acetate	130	259	389	734
Propanoate	7	15	22	126
Butyrate	1	2	3.5	
Boron	< 5	< 5	< 5	< 5
Cl:Br	1016	288	71	107
Cationic Species (mg/kg)				
Lithium	0.5	1.0	1.5	2.5
Barium	3	6	9	15
Strontium	8.8	17.6	26.4	44.0
Calcium	756	1512	2268	3426
Magnesium	15	30	45	864
Sodium	3116	6232	9348	17324
Potassium	186	372	558	1001
Iron	15	30	45	75
Copper	< 1	< 1	< 1	< 1
Zinc	1	2	3	5
Manganese	3.1	6.2	9.3	15.5
Aluminium	< 5	< 5	< 5	< 5
Elements (mg/kg)				
Phosphorus	< 3	< 3	< 3	< 3
Silicon	2	3	4	5
Sulphur	< 10	17	26	116
Total chloride equivalent (mg/kg)	6362	12804	19374	35662
Total sodium equivalent (mg/kg)	4144	8287	12431	23591
Total sodium chloride equivalent (TDS) (mg/kg)	10506	21091	31805	59253
Cation/Anion Balance	100.44%	99.82%	98.95%	102.02%
Cation/ Anion Bias	0.44%	-0.18%	-1.05%	2.02%

Is there any need to preserve the samples?

Once depressurised a water sample may undergo several changes before it reaches an equilibrium position. If the requirement is to approximate the original composition as closely as possible then there are several preservation steps that can be taken to ensure sample integrity. Samples for cations and metals can be preserved with concentrated nitric acid to reduce precipitation of metal species such as iron. Samples for organic acid anions (VFA) may be preserved with concentrated potassium hydroxide to prevent microbial activity. When preserving samples it is important to appreciate that the volume of acid or alkali added should not be so large that it dilutes the sample significantly. As a guide, volumes added should be of the order of 1-3 drops per 100 mL sample.

How long does it take?

The analyses and reporting of results should normally be completed within 10 working days. In exceptional circumstances faster turnarounds may be possible, but this is dependent on the workload at the time and availability of staff and equipment. A surcharge may be levied to accommodate faster turnarounds dependent on the specific requirements.