

# **ALTERNATIVES TO CONVENTIONAL TECHNIQUES FOR QUANTIFYING LIQUID FLUIDS CONTENTS ON LARGE BATCHES OF BITUMEN-SATURATED SAMPLES**

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## **ABSTRACT**

Measuring in-situ oil and water contents on core samples is routinely performed in the laboratory. Two extraction techniques are mainly used in petrophysical labs: the "Retort" and the "Dean Stark". Despite differences in the way the oil content is derived, similar results can be obtained with both methods once appropriate corrections are applied.

However, alternative methods are routinely used in organic geochemistry, some of which proved very cheap and fast techniques.

One of these methods is based on the so-called "Solid-Phase Extraction" SPE process, and is particularly interesting for several reasons:

- Time and labor savings, and increased samples throughput: several commercial solutions are available on the market, and come in the form of easy-to-use, compact and automated pipetting robots, able to perform extractions on up to 480 samples per day, thus resulting in cheap analysis unit price.
- Low temperature extraction: measurements are performed at ambient temperature (no risk of pyrobitumen formation like with Retort pyrolysis),
- Safe and healthy environment with limited environmental footprint: extractions are done with minute quantities of solvents.

We present a case study where all these considerations (transportability / HSE / time / cost) were critical in selecting the SPE process for quantifying oil and water contents on large batches of bitumen-saturated core samples (> 17,000 samples). Comparison on a few QC samples of oil content measurements between SPE and classic Dean Stark experiments proved quite satisfactory.

## **INTRODUCTION**

Several lab techniques can be used to separate and quantify fluids from an impregnated rock sample. Whatever the technique used (e.g. Retort or Dean Stark), it is generally possible to obtain comparable and reliable results once calibrations and corrections appropriate for each method are applied.

However, accuracy is not always the only consideration at stake when comparing different types of experiments. In particular, both experiment duration and analysis unit cost may become important issues when the quantity of samples analysis to perform becomes very large. It may also be more convenient to perform the fluid analysis in a brand-new facility close to the coring site; in such case, equipment transportability and footprint will be important considerations and HSE will obviously become a chief concern (e.g. solvent supply chain, handling and disposal), particularly if operating in a remote area.

## **INCENTIVES TO TEST AN INNOVATIVE ANALYSIS DEVICE**

We thus present a case study concerning a bitumen mining project, in which HSE, equipment transportability and time were critical issues, leading to selection of an innovative analysis technique alternative to those classically offered by commercial labs. The project consisted in coring a total of 130 shallow wells over 2 years; more than 150 m of core were expected to be recovered per day (2 rigs), and we anticipated that up to 300 measurements of bitumen contents would have to be performed daily, and possibly more than 17,000 measurements over the whole campaign.

Having considered all the technical options available on the market to perform large batches of bitumen extraction and content measurement in short times, we selected the so-called ASPEC technique (Automatic Solid-Phase Extraction Cartridge), because of its short experiment duration (3 minutes / sample), high sample throughput (up to 480 analysis per day and per apparatus), limited solvent consumption (3 ml / analysis) and low unit cost (10 US\$ / analysis). Furthermore, being performed by an automated robot, the extractions result in dramatic reduction of solvent use (HSE), footprint (no hood required since small quantities of solvent in closed system) and sample handling times, as well as improved sensitivity and reproducibility.

Prior to presenting the results of the ASPEC measurements campaign and how good they compare with conventional techniques that are more costly and lengthy, we will list the different fluid extraction and assay techniques available on the market, along with their respective advantages and inconveniences.

## **FLUID EXTRACTION AND ASSAY TECHNIQUES**

We have summarized in Table 1 the different potential techniques which can be used to extract and quantify fluids contents from a rock sample, keeping in mind that our main focus will be on bitumen quantification.

### **Types of extractions processes**

Two main separation processes are used in commercial labs to extract fluids from an impregnated rock sample:

- Distillation: the fluid property on which the process is based to segregate the components is volatility (ability to vaporize).
- Solvent extraction: the fluid property on which the process is based to segregate the components is solubility.

Techniques listed in Table 1 are based on 1 of these processes, or a combination of both.

### **Types of fluids collected**

Extracted fluids may be collected for direct volume or mass quantification, or may just be extracted and discarded (depending on apparatus design), in which case, 1 of the 2 the fluid contents has to be derived through indirect mass-balance calculation. Whether the fluid content is directly measured or indirectly calculated is listed in Table 2.

The only technique prone to mass-balance errors on oil content determination is the Dean Stark, first, because of potential sample material loss in the flask, and second, because the quantification of apparent extracted water may be biased by several factors.

These potential biases are detailed in the quite comprehensive brochure "Recommended Practices for Core Analysis, Feb. 1998" by the American Petroleum Institute (ref.<sup>1</sup>) and will not be further considered. However, for the specific case of bitumen with a boiling point in excess of 200°C, some modified Dean Stark techniques have been developed which allow a direct quantification of the bitumen content rather than by an indirect mass-balance calculation (see ref.<sup>1</sup> and ref.<sup>2</sup>).

### **Plus and Cons of each lab technique**

With reference to Table 1 (again, the API brochure (ref.<sup>1</sup>) is a quite exhaustive reference document):

#### **ASPEC:** (Automatic Solid-Phase Extraction Cartridge)

- The main asset of this "solvent extraction" technique is the fact that the ASPEC device is an automated pipetting robot with a high sample throughput (Figure 1):

- Experiment duration is only 3 minutes per sample,
- The device can be equipped with racks of up to 180 sample cartridges, programmable in a row and with no further technician maintenance, resulting in improved sensitivity and reproducibility.
- In the basic configuration, the 180 analysis are sequential (but up to 4 measurements can be made in parallel on the top end manufacturer devices), that is, a sample throughput of up to 480 measurements per day and per apparatus according to the manufacturer.
- Only a small quantity of solvent is used for each extraction (3 ml per sample),
- The unit cost is very attractive, around 10 US\$ per sample.
- The very short duration of each analysis (3 minutes) makes it very attractive when having to conduct quick QC's or tests and get almost immediately the results without having to wait 45 minutes (Retorts) or even several hours (Dean Stark) before validating or invalidating the measurement.

**ASE:** (Accelerated Solvent Extraction)

- This "solvent extraction" technique (Figure 2) presents similarities with ASPEC.
- The main difference is that the extraction can be made under pressure and temperature (up to 100 bar and 100 – 200 °C), which improves the solvent penetration. This may prove useful for tight samples.

**Retort:**

- The technique is based on "distillation", and as such does not use solvent. A side-effect of the high temperatures (up to 650°C) generated by the electric heating is that it results in the crystallization waters breaking down, and in an irreversible destructive chemical decomposition, (i.e. pyrolysis) of the organic material which either yield too low of an apparent oil content (if the heating process cracks the oil, a coking effect) or too high of an apparent oil content (if solid organic matter, e.g. kerogen, is present and breaks down at high temperature).
- The sample throughput is attractive, 320 measurements per day per apparatus.
- However, we discarded this method as a possible routine technique for our case-study "bitumen measurements campaign" for 3 reasons:
  - The risk of emulsions between oil and water in the collecting tube,
  - The pyrolysis of the bitumen which would made any further compositional analysis unreliable,
  - The need for regular corrections and calibrations to the apparent recovered oil and water volumes (Figure 3), due to the side-effects of pyrolysis.

**Dean Stark:**

- This is a mixed "Distillation (for water) – Solvent extraction (for oil)" method. Boiling toluene (111°C) is used as the solvent.
- Advantage of the method is direct water content measurement.
- The main inconvenience of the method is the duration of the experiment: the extraction takes at least several hours on crushed material (and days on regular plugs). This is not a problem in itself as certain commercial labs have equipped rooms with 100's of individual cells capable of treating several 100's of measurements per day (on crushed samples); however, the footprint impact and HSE constraints (around 1 liter of solvent for each cell) are such that only specialized labs can afford such facilities.
- As such, we had to disqualify the Dean Stark method as a routine method to treat our potential 17,000 bitumen extractions. The second reason to discard the Dean Stark as routine being the measurement unit-cost, far less attractive than for the ASPEC (10 US\$ for the ASPEC (manufacturer website), vs. 75 to 100 US\$ for the Dean Stark (commercial labs, on crushed samples)).
- However, we kept the Dean Stark method as a quite valuable method to perform QC tests of our ASPEC measurements and equipped the local brand-new lab with 7 Dean Stark cells to perform some QC's at random.

**Rock-Eval:**

- We considered this method when investigating fluid extraction alternatives; it was soon discarded for 3 reasons:
  - Duration of the experiment, ~ 1 hour,
  - Mass of the Rock-Eval sample, 25 mg (milligram) only, and then concern about the sample representativity,
  - And, like for Retort, pyrolysis of the bitumen which would make any further compositional analysis unreliable.
- Though an invaluable method to characterize the S1 / S2 spectrums, it didn't prove applicable to our context and the expected sample throughput (up to 300 per day).

Considering all these alternatives versus our constraints (300 analysis per day, up to 17,000 analysis overall, results expected almost in real-time), we opted for the ASPEC method in routine, plus Dean Stark and ASE to perform occasional QC. We first describe some of the ASPEC – ASE features, then the results of the measurements campaign.

**ASPEC - ASE EXTRACTIONS METHODS**

ASPEC (Automatic Solid-Phase Extraction Cartridge), pictured on Figure 1, is a device manufactured by Gilson, exploiting the so-called Solid-Phase Extraction SPE process.

SPE is a process presenting analogies with elution chromatography, in which a solid "stationary phase" located within an extraction cartridge (Figure 9) adsorbs preferentially some compounds from a mixture during a process involving several steps (Figure 10).

One interest of the ASPEC is that this is an automated pipetting robot with reduced footprint (height ~ 60 cm), equipped with racks containing up to 180 SPE cartridges and their collecting tubes beneath. A mobile X-Y-Z arm (cf Figure 1) can displace over each cartridge to perform the 4 steps schematized on Figure 10. Benefits of automation are dramatic reduction of solvent use (HSE), footprint (no hood required since small quantities of solvent in closed system) and sample handling times. Higher sample throughput with improved sensitivity and reproducibility are other benefits. Solvent and labor costs are reduced by up to 90%.

In our present lab application, it is not the SPE process (adsorption) in itself that we exploit, but the fact that the microporous stationary phase will let pass through the mixture of oil and solvent while retaining the solid grains above. The protocol is described here: a fresh rock sample (mini 5 g) containing oil and water is first ground to medium to fine-grained size, this to facilitate the solvent percolation in the sediment and extraction efficiency during the SPE process. It is then put in an oven to dry at 45°C for 12 hours, this to evaporate water (which can be quantified through mass-balance at this stage), leaving only oil in the sediment. The SPE extraction cartridges are then loaded with the dry fine-grained sediment containing the oil, oil which is then extracted under pressure by DCM dichloromethane solvent, while the clean oil-free sediment is retained on top of the sintered frit material of the cartridge stationary phase, material which pore diameter is ~ 20 µm (it is then important not to grind the rock below ~ 100 µm so as to prevent any risk of fines plugging the frit material). The percolating mixture of oil and solvent is then recovered in a collecting tube beneath, and the oil content quantified by evaporating the solvent at 45°C for 12 hours then 60°C. We use DCM dichloromethane as solvent, first due to its ability to efficiently dissolve a wide range of organic compounds (oil, resins) and second, because of its high volatility / low boiling T° (40°C) which makes DCM ideal to separate solvent from bitumen by low T° evaporation.

ASE (Accelerated Solvent Extractor), pictured on Figure 2, is a device manufactured by Dionex, exploiting the so-called Accelerated Solvent Extraction process. Here, the solvent extraction (by dichloromethane) is performed at 100 bar and 100°C to 200°C, which improves the penetration of matrix by solvent and also the kinetics of the extraction process, which leads to a better percolation of the solvent (may be useful for tight samples). Up to 24 samples can be extracted sequentially with the ASE extractor

which can process samples from 1g to 100g in a few minutes.

## **RESULTS OF THE ASPEC CAMPAIGN**

### **Preliminary feasibility**

Prior to ordering the ASPEC device and lay out of the associated lab facilities, we had to make sure the technique was appropriate for our specific bitumen project.

We already had a successful experience with its cousin, the ASE device, on a conventional oil field (Figure 4), where the oil saturations derived from conventional Dean Stark and ASE proved extremely similar. But now, we were going to deal with bitumen, and the ASPEC is an extraction at ambient temperature only (20°C). How efficient would be the extraction?

We did the feasibility on an old well drilled decades ago on the mine, and the first thing to do was to compare the composition of the extracts between the ASPEC (extraction at 20°C) and ASE (extraction at 100°C and 100 bar). As can be seen on Figure 5, the Iatroscan extracts proved quite similar on the 2 samples we tested. We used dichloromethane as solvent in both cases, for its ability to efficiently dissolve a wide range of organic compounds (oil, resins).

### **Confirmation of the ASPEC potential on the first cored wells**

The next step was to confirm the ASPEC reliability on the first new wells that get cored:

- First, we checked that the repeatability of the device was up to the standards (Figure 6 left); we also checked that the size at which the rock was ground – fine or medium – only had a limited impact (Figure 6 right).
- Then, having passed these tests, we cross-checked the results of the ASPEC extractions (at 20°C) with other methods on twin plugs versus ASE (extraction at 100°C) on Figure 7 left, and versus conventional Dean Stark (extraction at 111°C) on Figure 7 middle. The correlations appear quite satisfactory.
- We did also a quick QC (Figure 7 right) of oil content calculation by mass-balance between the dry rock sample mass before and after oil extraction. By experience, we know that this method is less accurate, particularly when volumes to determine are small, and that's what we observed on Figure 7 right. We however systematically computed the mass-balances as a rough QC to detect possible anomalies.

Note that on all the plots, the bitumen contents are expressed in mass % of the mass of bitumen versus the impregnated dry rock mass (i.e. with bitumen but without water, as this is one standard in the mining industry).

### **At random QC's during the routine ASPEC campaign**

Approximately every 100 ASPEC measurements, a random QC was conducted on a twin sample with a second spare ASPEC device (independent device, calibrations and blank corrections) to check that there was no drift or bias of the ASPEC analysis with time; the test is conclusive as can be seen on Figure 8 left. Similarly, approximately every 20 ASPEC measurements, a random Dean Stark measurement was conducted on a twin plug. Again, the plot on Figure 8 right shows that the test proved quite satisfactory (taking into account the "twin" samples were never perfect twins), confirming the reliability of the ASPEC method as an operational routine lab technique.

## **CONCLUSIONS**

- 1) We presented a case study in which the potential of a bitumen mining project had to be quickly evaluated, with 100's of bitumen content analysis having to be performed daily (and 17,000 of analyses over the whole coring campaign) and locally in the host country. With such constraints, screening of the conventional commercial techniques led to the conclusion that new innovative techniques had to be looked for.
- 2) The ASPEC technique, used in organic chemistry, proved the best candidate. The comparison of bitumen measurements with standard techniques on twin plugs confirmed the potential, and the whole ASPEC campaign proved a success, with quite reliable results, at a quite low cost (10 US\$ / sample) and low level of technician supervision (automated pipetting robot autonomous once programmed to run the 180 analysis).
- 3) The technique has been implemented on a conventional oil field as well and again proved quite satisfactory.

## **ACKNOWLEDGEMENTS**

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## **REFERENCES**

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2. "Alberta Oil Sands Index (AOSI)-3573, Round Robin Study of Analytical Procedures of Various Laboratories on Assay Analysis of Athabasca Tar Sands", *AOSTRA Information Center, 1974*.
3. Zimmermann, B., Papagiannopoulos, M., Mellenthin, A., Krappe, M., Maio, G., and Galensa, R., "Coupling of ASE, ASPEC and HPLC – Automated Determination of Proanthocyanidines in Malt", *G.I.T. Laboratory Journal, Apr. 2002*.



		Duration measurement	Unit Cost per measurement	Volume solvent per measurement	Mass sample	Condition P - T°	Advantages	Inconvenients
<b>ASPEC</b>	Solvent Extraction	<b>3 min</b> (180 cells/apparatus, sequential = 480 measurements per day & apparatus,	<b>10 US\$</b> (manufacturer website)	<b>a few ml to 10 ml</b>	<b>1 to 5 g</b>	. Atm . 20°C	- Quick experiment (interesting for repeatability & QC) - Automated robot - Direct & accurate measurement of Oil content - Small quantity of solvent used	- Indirect calculation of Water content (mass-balance)
<b>ASE</b> (same use as ASPEC; more appropriate for lower perm k samples)	Solvent Extraction	<b>15 min</b> (24 cells/apparatus, sequential = 96 measurements per day & apparatus,	-	<b>a few 10's of ml</b>	<b>10 to 20 g</b>	. 100 bar . 100°C (to 200°C)	- Direct & accurate measurement of Oil content - Small quantity of solvent used	- Oil and Water volumes need corrections - Distilled volumes may form emulsions - Bitumen pyrolysis at 650°C (compositional analysis no more relevant)
<b>Retort</b>	Distillation & Pyrolysis	<b>45 min</b> (10 cells/apparatus, parallel = 320 measurements per day & apparatus,	-	no solvent	<b>100 to 175 g</b>	. Atm . 175°C to 650°C	- Fast and direct measurement of both Oil and Water contents - No solvent	- Oil and Water volumes need corrections - Distilled volumes may form emulsions - Bitumen pyrolysis at 650°C (compositional analysis no more relevant)
<b>Dean Stark</b> (on crushed sample)	Distillation & Solvent Extraction	<b>~ 8 h</b> = 3 measurements per day & apparatus,	down to <b>75 - 100 US\$</b> (in commercial labs)	<b>~ 1 liter</b> (recycling possible in some cases)	<b>20 to 100 g</b>	. Atm . 110°C	- Direct & accurate measurement of Water content	- HSE (solvents) & footprint - Experiment duration - Indirect calculation of Oil content (mass-balance) - Care needed (to account for potential mass-balance bias)
<b>Rock-Eval</b>	Pyrolysis	<b>1 h</b> = 24 measurements per day & apparatus,	-	<b>&lt; 1 ml</b>	<b>25 mg</b>	. 650°C	- Characterization of S1 & S2 spectrums	- Representativity of 25 mg of sample ? - Experiment duration (compared to ASPEC) - Bitumen pyrolysis at 650°C (compositional analysis no more relevant)

ml = milliliter; g = gram; mg = milligram

Table 1: Lab techniques for quantification of fluid contents on rock samples

- Both Oil and Water collected and measured	- Retort - Modified Dean Stark
- Only Oil collected and measured - Water derived by Mass-balance calculation	- ASPEC & ASE
- Only Water collected and measured - Oil derived by Mass-balance calculation	- Routine Dean Stark - Karl-Fisher

Table 2: types of fluid measured for each extraction technique

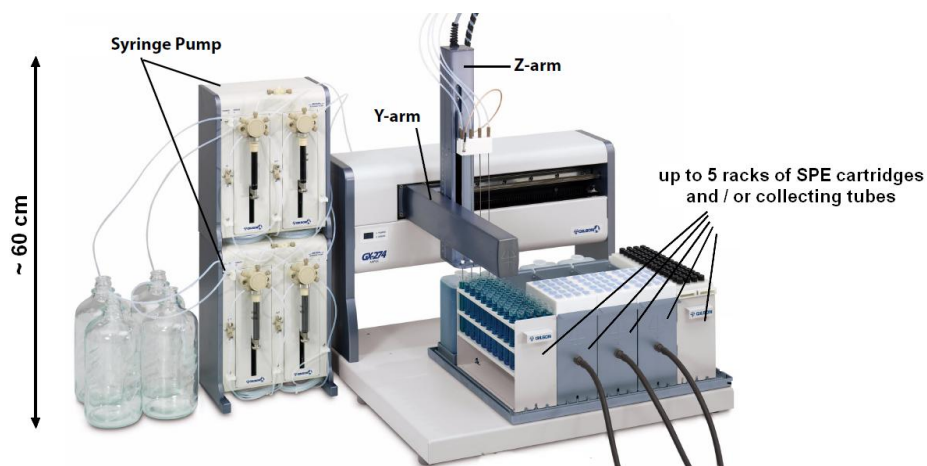


Figure 1: SPE device type GX-274 ASPEC™ by Gilson



Figure 2: ASE device type ASE 350™ by Dionex

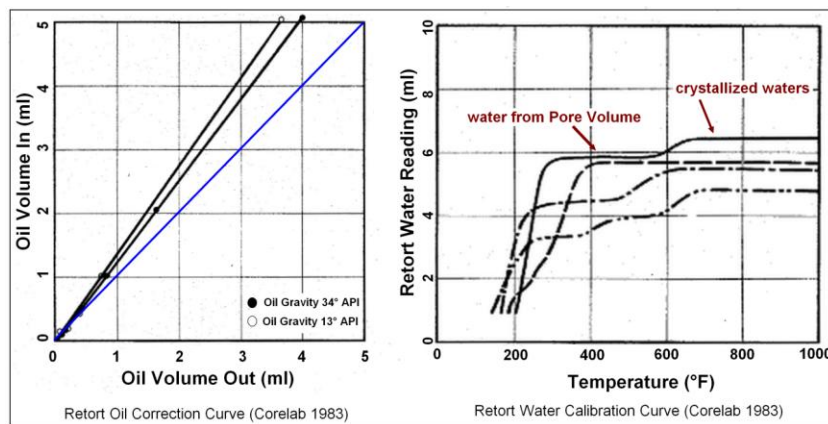


Figure 3: oil and water corrections / calibrations with Retort

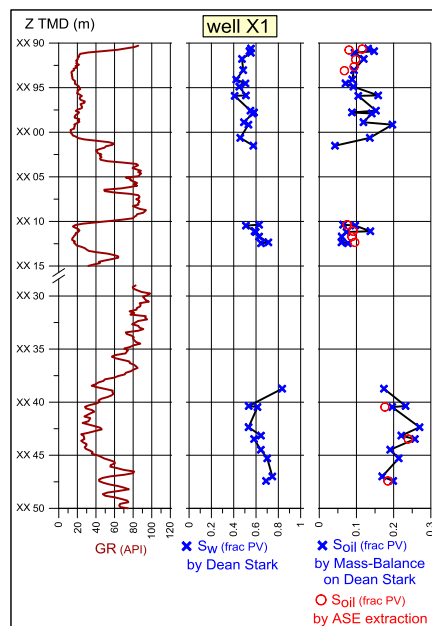


Figure 4: Comparison of ASE and Dean Stark oil extractions on a cored well (conventional oil field)

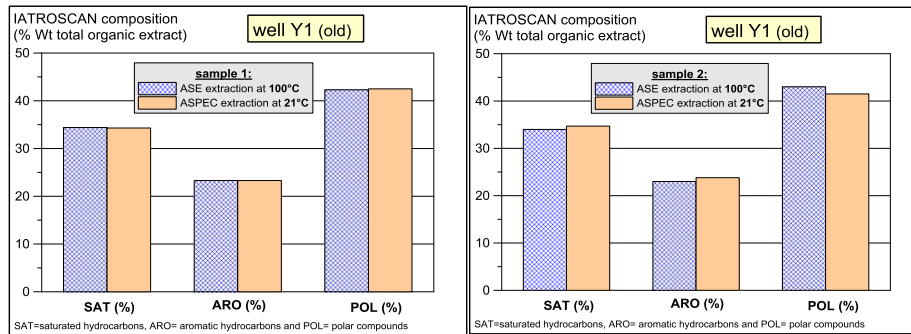


Figure 5: Comparison of ASPEC and ASE Iatroscan composition

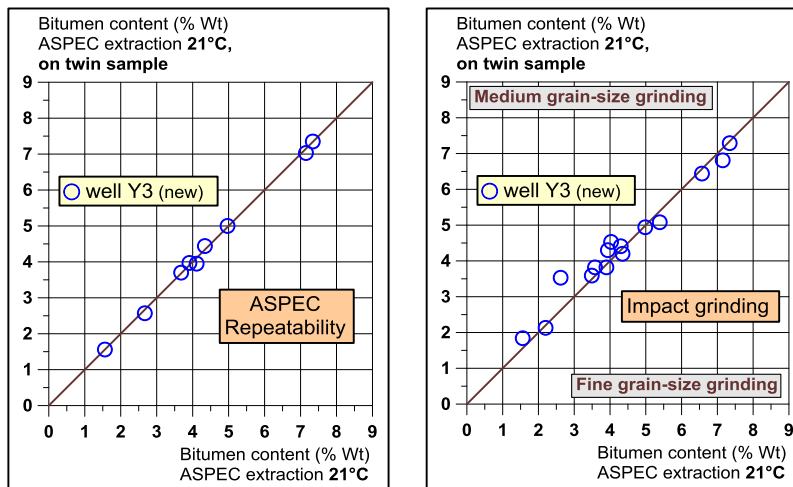


Figure 6: ASPEC setting-up

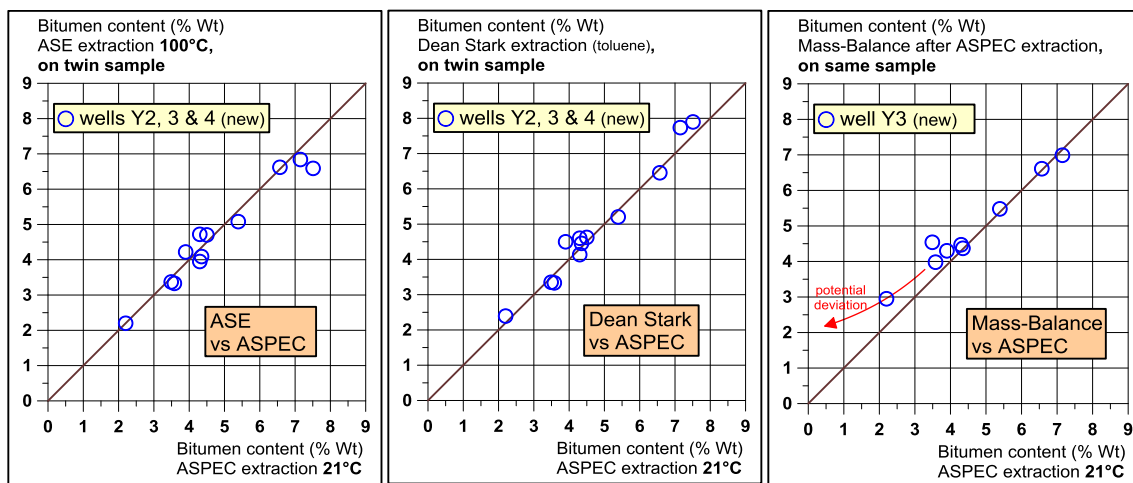


Figure 7: x-check ASPEC results with other techniques

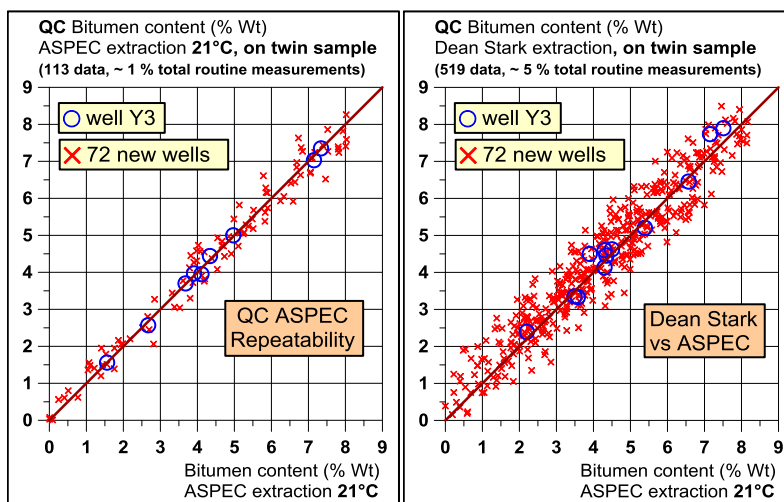


Figure 8: ASPEC, routine measurements



Figure 9: SPE cartridges

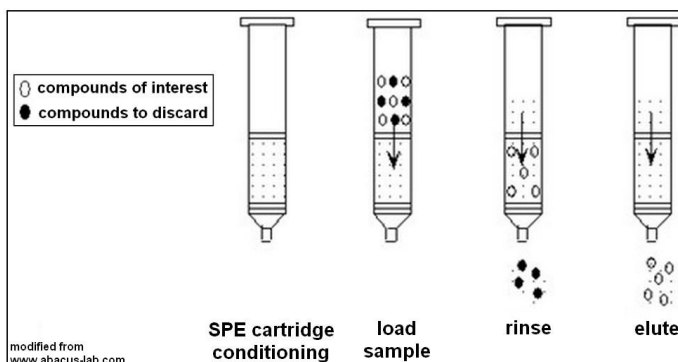


Figure 10: the 4 steps during SPE process