



**The Quest for a Quantitative Jet Fuel
Contamination Limit—Particle Counting
“RESOLVED”**

**Vic Hughes & Paula Zard
Particle Solutions Ltd.**

INTRODUCTION

Until recently, jet fuel cleanliness as a product quality (PQ) parameter was expressed only in terms of a subjective, visual assessment (Clear & Bright). A gravimetric method was, and still is, invoked in some product transfer agreements and especially in military fuel handling. This latter method only measures particulate matter and takes many hours to produce a result. Not only that, many operators in the industry are aware that the results obtained are often in error.

Clearly there was a need for a more objective, quantitative, timely and reliable methodology for assessing jet fuel cleanliness – after all we are now in the 21st Century – and especially one that can pervade the industry to yield a common terminology from refiner to airline operator. Previous papers^{1,2} identified particle counting as an appropriate contender. As a method that had already reached maturity within other hydrocarbon industries it had the advantage of being an “off the shelf” solution. Nevertheless, it required a cross-industry approach to tailor the ISO11171-type of technology used in Automatic Particle Counters (APC) to the needs of jet fuel.³

Once jet fuel parameters had been determined, the next stage in the development of this methodology was to arrange extensive field trials. Building an extensive data set for jet fuel at various points in the distribution system demonstrated that the methodology was not only meeting the PQ need but was surprisingly useful in terms of condition monitoring and process optimization^{4,5}.

AVIATION JET FUEL APC

As a result of the above activities it became clear that the range of particle sizes encountered in the jet fuel system was much tighter than in hydraulic fluids – for which the

original ISO11171-type instruments were designed. It was therefore proposed and accepted by the industry that jet fuel APCs need only measure up to about 20µm(c) for particulate. However, water droplets, included in the counts, range in sizes larger than this and by empirical reasoning an upper limit for measurement was set at >30µm(c). The lower limit of 4µm(c) is set by the APC test method capabilities.

Jet Fuel particle counting sizes, µm(c)					
≥4	≥6	≥14	≥20	≥25	≥30

Given this size range and generally encountered particle counts work then concentrated on formalizing Jet fuel test methods under the auspices of The Energy Institute which now has three particle counting methods included in its Test Methods portfolio – IP564, 565 and 577. They all produce the same analysis but the slight procedural differences relating to individual APCs is one reason preventing the adoption of a single generic method.

**ADOPTION BY JET FUEL
SPECIFICATIONS**

On 8th April 2008, Def Stan 91-91, The UK MoD Specification for Turbine Fuel, Jet A-1, Aviation Kerosine, NATO Code: F-35 Issue 6 was issued with a requirement to “report” particle counts using one of the IP test methods. Note 4 in that specification read:

“The implementation date for particle counting is 30th June 2009, but where possible, to help the data collection process, the results should be reported before that date. It is the Specification Authorities intention to replace Test 1.3 (gravimetric) with Test 1.4 (particle counting) at the earliest opportunity.”

This was followed in July 2008 by the adoption of the same requirement in Issue 23 of the Joint Inspection Group (JIG) Product Specifications.

It was felt by the industry that a period of data gathering should precede any discussions on limits, hence the “report only” requirement. Furthermore the requirement only applied at point of manufacture – role out downstream would have to await resolution of the point of manufacture limits – but it is a stated intention.

THE FIRST DEF STAN 91-91 JET FUEL DATA SETS

At the Aviation Fuel Committee meeting held in London in March of this year, the first data set was presented⁶. After rejecting sample data that was incomplete (no batch number, no gravimetric comparison etc), there were 650 data sets from 5 sources representing over 14 refineries. It soon became clear that many fuels had high counts (>2500/ml for >4µm(c)) whilst returning gravimetric results well within the limit of 1mg/l. Whilst the gravimetric results do not necessarily have to correlate with particle counts, the differences were dramatic. Many fuels indicated broad distributions with significant counts in the >20µm(c) size range and this strongly suggested the presence of water droplets. This would also explain the very poor correlation with gravimetric assays that only include particulate matter.

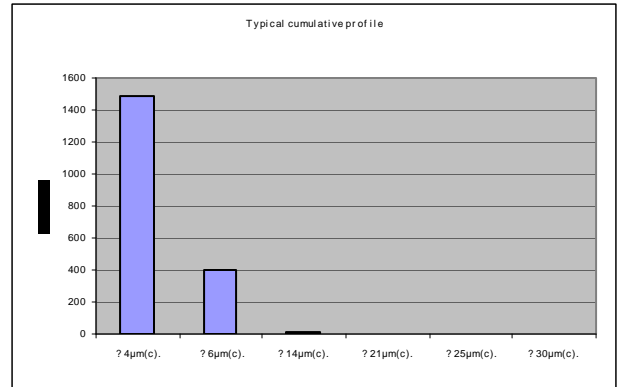
Amongst a number of planned “next steps” was one that has identified the need to try to separate particulate counts from total counts that may include water droplets. There is a proposed particle counting limit based on the whole data set and the previous gravimetric percentage failure rate and that is ISO 4406 codes 19:17:14 for particle sizes >4µm(c), >6µm(c) and >14µm(c). But this would be a forced fit to the data and when compared to earlier field data^{4,5} would be far too relaxed as a limit.

SEPARATING WATER DROPLET AND PARTICULATE COUNTS

Natural systems characteristically display a log/normal pattern in terms of size distributions with very large numbers of small particles and less of the larger particles.

There are estimates that suggest a billion times more photons than atoms. There are many orders of magnitude more people than cities, sand grains than beaches, and, happily, bottles of beer than drinkers.

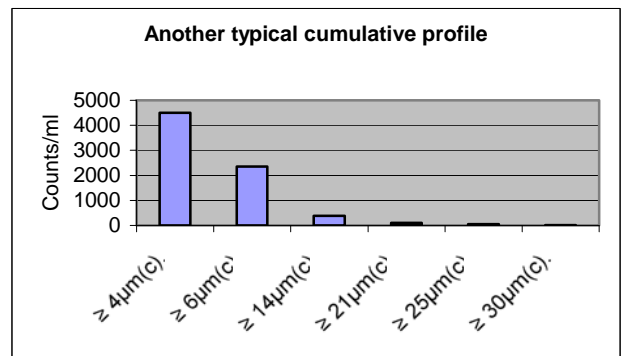
The majority of data points in the Def Stan data set indicated the expected log/normal distribution as shown in Figure 1.



µm(c) Particle Count per ml /ISO 4406					
≥4	≥6	≥14	≥20	≥25	≥30
1486	402	15	2	0	0
18	16	11	8	6	4

Figure 1. Log/normal distribution common in Def Stan 91-91 data set

Most of these samples also yielded much lower total counts (<<2500/ml) and were typical of samples previously encountered throughout most of the jet fuel distribution system during the field trialling stage of the APC development.



µm(c) Particle Count per ml /ISO 4406					
≥4	≥6	≥14	≥20	≥25	≥30
4501	2357	379	103	46	19
19	18	16	14	13	11

Figure 2. Atypical distribution encountered in Def Stan 91-91 data set

Most of the high-count data in the Def-Stan set did not have a simple log/normal distribution – see Figure 2. Both typical and atypical distributions gave similar (low) gravimetric assays. The conclusion is that the atypical distribution is likely to also contain water droplets and these present a significantly different size distribution to particulate¹. (Another way of expressing this would be to say that the distribution is the result of a number of superimposed distributions – one of which may be due to water droplets.)

One solution to this problem would be to remove the water droplets whilst not affecting the particulate size distribution and this is the course of action favoured at this time.

OPTIONS FOR SEPARATING WATER DROPLET COUNTS FROM TOTAL COUNTS

Cosolvents

The use of a material that has solvency in both hydrocarbon and aqueous phases has the potential to solvate any free water in the hydrocarbon – a cosolvent. To get more water into the fuel the solvent has to be more polar than the fuel, and, the more polar the solvent the less soluble it will be in the fuel – so compromise! The parameter governing this process is the Partition coefficient P given by:

$$\log P_{\frac{oil}{water}} = \log \left(\frac{[cosolvent]_{oil}}{[cosolvent]_{water}} \right)$$

e.g. P (methanol) = -0.83 between water and octanol.

The use of toluene and isopropanol as solvents for the removal of water contamination in a particle counting fluid has been previously suggested by Mountain et al⁷. A treat ratio of 1:1 with the test fluid is recommended.

¹ Whilst particulate can exist as ever increasing numbers of ever decreasing size (right down to the molecular level), free water cannot exist at very small sizes due to thermodynamic effects associated with the high local energy produced within a very small surface radius of curvature. Water droplets therefore have a finite “smallest size” and there are driving forces (Ostwald diffusion and auto-coalescence) to attain a secondary emulsion size range that happens to be of micronic dimensions.

Whilst this may represent a way forward for lubricant analysis, the addition of such large volumes of cosolvent to a sample of jet fuel will significantly alter the state of any aggregated particulate.

For smaller volume treatments of jet fuel, Clark and Crichton advocated the use of a range of cosolvents including alcohols and glycols but also many others⁸. When tested practically, results were of mixed success when using isopropanol with jet fuel. There is also conflicting information about this proposed method in the literature^{9,10}. Our own work showed that in jet fuel, the partitioning for the cosolvent lies towards the water phase producing particle counts as follows:

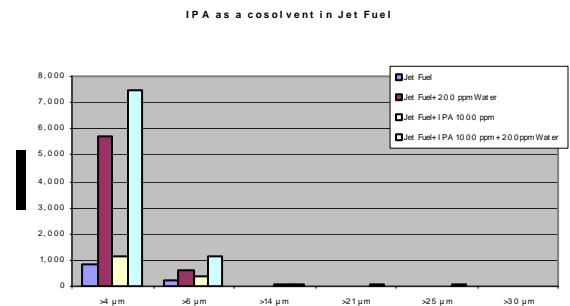


Figure 3. Particle counts for Jet fuel containing water droplets and/or isopropanol cosolvent.

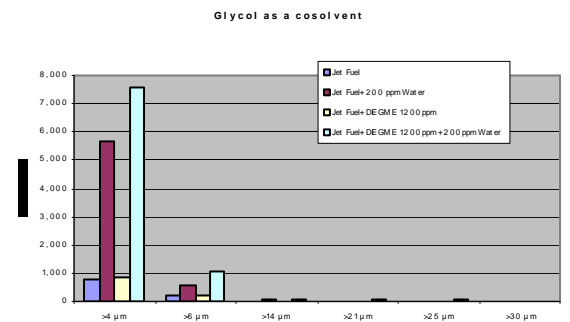


Figure 4. Particle counts for Jet fuel containing water droplets and/or a glycol cosolvent.

Whilst it's clear there's a huge difference in apolar character between actual fuels and the more academic systems reported in the literature, the Energy Institute is planning to continue to investigate the cosolvent possibility.

Nano-encapsulation – Revisited?

Liquid fuels containing water droplets and particles with sizes << wavelength of light will appear isotropic – i.e.

single phase. Encapsulation of the free water within molecular structures with dimensions less than 500nm will render the water invisible to light detection generally and to light obscuration in particular. This is not a new approach. A report dating back to the earliest emergence of civilization utilized this approach using Aerosol OT – a sulphosuccinate¹¹.

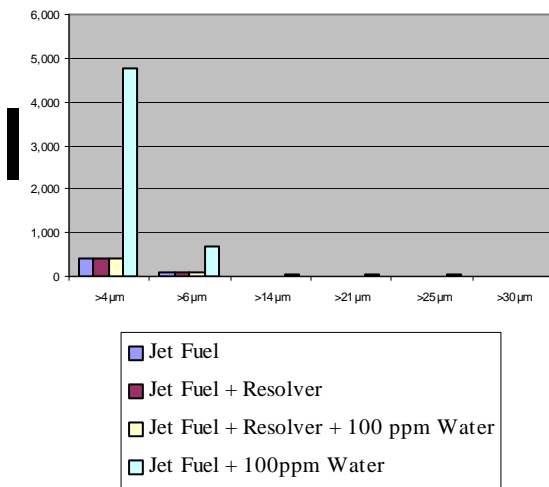
This is the authors' favoured route – provided we can be assured that the process does not significantly alter any particulate aggregation that would be characteristic of the sample – that means low shear and low volume processing.

The previous AOT work had identified many of the issues with this procedure but the one that we would add to the “low shear” and “low volume” would be “middle distillate fuel compatibility”.

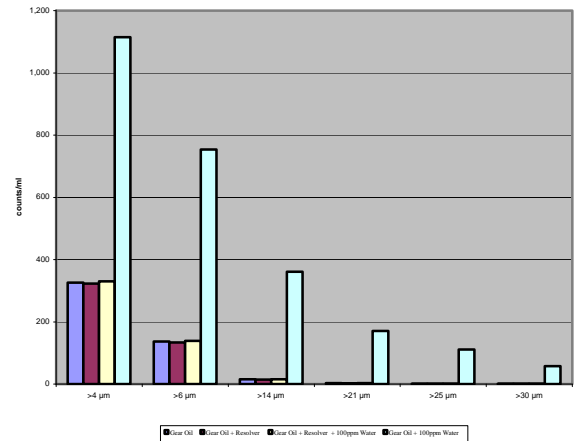
The particular combination of surfactants and cosurfactants (proprietary) that we have incorporated into the particle counting water droplet correction fluid (tradenname – Resolver) takes account of middle distillate compositional variations, temperature variations and is matched volumetrically with water challenge. In this latter respect the modus operandi would be to overdose the sample with Resolver to ensure complete water encapsulation. The material is fully soluble in all middle distillate fuels including bio-derived types requiring only gentle agitation for full dispersion. Because it is of relatively low volume and “soluble” in the fuel, there is no significant volume change to the sample and so post measurement volumetric corrections are not required.

Examples of its use are as follows:

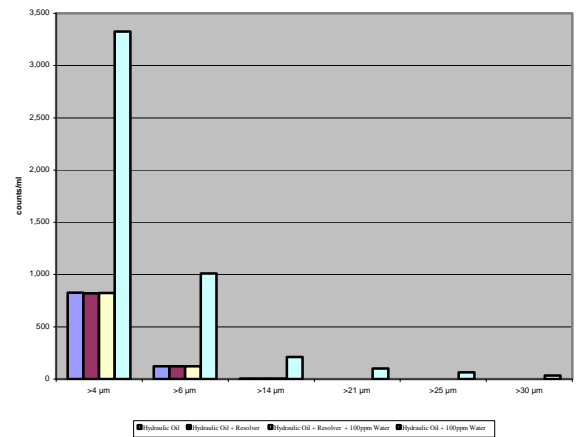
Jet A-1 Resolver example



Gear Oil Resolver example



Hydraulic oil Resolver example



Work thus far has shown full encapsulation of water droplets in a range of hydrocarbon liquids and across a reasonable temperature range.

In practice this enabling technology will permit the analyst to produce a “dry” particle count, but, with a little mathematical manipulation, there is also the possibility to carry out a “differential” analysis on the sample. This would simply be a procedure involving the analysis of Resolver-treated and untreated samples with the former yielding the “dry” count and the difference between the two results yielding water droplet counts.

NEXT STEPS

The Energy Institute has requested full validation testing of the two main contenders – cosolvency and

encapsulation. One of the most difficult aspects of this is ensuring the availability of water in fuel emulsions of known, fixed quality. This has been resolved by accessing an EI1581/83/90 full-scale aviation fuel test rig that can produce consistent volumes of fuel samples with known levels of dispersed water droplets. Shear regimes can also be changed to vary the droplet size distribution. Test dusts types and levels can also be introduced. A test matrix has been supplied to the relevant EI test methods panel and is awaiting agreement.

CONCLUSIONS.

Work on introducing a quantitative, objective, timely method to define jet fuel cleanliness has been almost a decade in its development. Particle counting proved ideal in having the required sensitivity in the size range of most interest to the industry. Extensive data gathering showed that limit setting would either have to make compromises and settle on an overall cleanliness code including both particulate and water droplets* – or – given enabling technology, deconvolute the total count result to yield a “dry” particle count and an optional water content.

The second option is now awaiting an Energy Institute validation programme.

An early resolution to the issue is expected, as limit setting is an extremely important and long-awaited development.

**(It’s worth noting that the gravimetric particulate limit in Def Stan 91-91 is 1mg/l compared with an IATA water limit of 30ppm, an order of magnitude difference and therefore very significant.)*

¹ Hughes, “Can a Quantitative Contaminants Specification be Realised for Jet Fuel?”, 5th IFC, 2002.

² Kitson-Smith et al., “Experience with the use of a particle counter in measuring fuel contaminants.” 9th International Conference on Stability, Handling and Use of Liquid Fuels, September 18-22, 2005.

³ Hughes et al., “Can a Quantitative Contaminants Specification be Realised for Jet Fuel? - Part II”, 6th IFC, 2004.

⁴ Hughes et al., “Aviation Turbine Fuel Particle Counting.” 7th IFC, 2005.

⁵ Kitson-Smith & Hughes, “The use of electronic sensors in field measurements of aviation jet fuel cleanliness.” 10th International Conference on Stability, Handling and Use of Liquid Fuels, October 5-11, 2007.

⁶ <http://www.dstan.mod.uk/afc%20presentations.html>

⁷ J.W. Mountain et al, US 6064480, Method of particle counting for water mixed lubricant, May 2000.

⁸ A.Q. Clark and J.S. Crichton, EP 1715323, Method for determining the concentration and/or size distribution of solid particles in middle distillate fuels, 2006.

⁹ S. I. Sinegubova, K. K. Il'in and D. G. Cherkasov.

Mutual Solubility of Components and Critical Solution Points in the System Water-Isopropyl Alcohol-*n*-Dodecane in the Temperature Range 5–120°C, Russian Journal of Applied Chemistry, Vol. 78, No. 3, March, 2005

¹⁰ T.M. Letcher and P.M. Siswana, Liquid-liquid equilibria for mixtures of an alkanol + water + a methyl substituted benzene at 25°C, Fluid Phase Equilibria, 74, pp203-217, Elsevier Science, 1992.

¹¹ B.M. Verdegan and L. Thibodeau, Particle counting oil and water emulsions, Particulate Science and Technology, 7, pp23-34, Hemisphere Publishing Corp., 1989.