# Characterisation of fume from hyperbaric welding operations

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Abstract. We report preliminary work characterising dust from hyperbaric welding trials carried out at increased pressure in a helium and oxygen atmosphere. Particle size and concentration were measured during welding. Samples for quartz and metal analysis and toxicity assessment were taken from a filter in the local fume extraction system. The residue of dust after metal extraction by nitric acid in hydrogen peroxide predominantly a non-metallic white powder assumed to be dust from welding rod coatings and thermal insulation material. Metallic analysis showed predominantly calcium, from the welding rod coating, and period 4 transition metals such as iron, manganese, magnesium and titanium (inductively coupled mass spectrometry, Agilent 7500c). The presence of zirconium indicated a contribution from grinding. The fume was nanoparticulate in nature with a mean particle diameter of 20-30 nm (MSI Inc WPS 1000XP). It showed an intermediate level of oxidative potential regarding the low-molecular weight respiratory tract lining fluid antioxidants ascorbate and glutathione and caused release of the inflammatory marker IL-8 in a human lung A 549 epithelial cell culture with no indication of cytotoxicity. The study findings have strong implications for the measurement techniques needed to assess fume exposure in hyperbaric welding and the provision of respiratory protection.

## 1. Introduction

In the offshore oil and gas industry there is a requirement to carry out welding on underwater pipelines. While in-water welding is possible it does not produce an adequate quality of weld and pipeline welding operations are carried out in a hyperbaric welding habitat. The worksite is enclosed in a metal container which is filled with a breathable gas mixture of helium and oxygen. The oxygen level in the habitat is held at between 30 and 40 kPa and so although oxygen partial pressure is higher than in air the concentration is very much lower at 2.7-3.6% at an illustrative depth of 100 metres of sea water. The divers who conduct the weld live on board a diving support vessel in chambers pressurised with helium and oxygen to the same pressure as the underwater workplace. They usually

work an eight hour shift and are transported from the vessel to the welding habitat in a diving bell. Occupational exposures are very difficult to assess under such conditions due to the remoteness of the work site. Each pipeline weld, however, is preceded by a trial weld conducted in a hyperbaric simulator onshore in order to demonstrate the competence of the welding team for insurance purposes. Such trial welds offer a practical opportunity to study hyperbaric workplace exposures.

Fume generation is an inevitable consequence of welding operations and such fume was considered a "nuisance" dust. More recently, however, it has been understood that welding fume does have a significant level of toxicity and UK legislation requires that its individual constituents are considered when calculating tolerable workplace exposures. High manganese exposure can lead to a Parkinsonoid condition of manganism [1] and welders are at risk from pneumonia [2] and ischaemic heart disease [3]. Divers who weld are also more likely to express cognitive symptoms [4]. Accordingly, we have carried out some work to characterise hyperbaric welding fume and report on the metallic content and cytotoxicity of dust from hyperbaric welding operations and its oxidant potential with preliminary work on the assessment of particle size.

## 2. Methods
The methods were applied during several different welding trials (Table 1).

**Table 1.** Analysis methods used for each welding trial

| Sample | WF001 | WF002 | WF003 | WF006 | n/a |
|---|---|---|---|---|---|
| Welding trial | 1 | 2 | 3 | 4 | 5 |
| Silica | Yes | Yes | | | |
| Metal | Yes | Yes | Yes | Yes | |
| IL-8 | Yes | Yes | Yes | Yes | |
| Cytotoxicity | Yes | Yes | Yes | Yes | |
| Oxidant potential | Yes | Yes | Yes | Yes | |
| Particle size | | | | | Yes |

### 2.1. Welding
While a limited amount of tungsten inert gas welding was carried out the greater part of the welding was conducted by manual metal arc welding (MMAW). Grinding was carried out using zirconium containing abrasive wheels. The weld piece was heated and lagged externally when heating pads were in use. Local fume extraction was used. The extraction system recirculated chamber atmosphere through a series of filters and chemical absorbents to remove the particulate and gaseous components of the welding fume. In addition to the local extraction system, welders wore respiratory protection equipment which was either a positive pressure respirator (Aga) or a particulate respirator (3M) and reflected the appreciation of risk of two different diving companies. The welding habitat was a cylindrical chamber with domed ends having nominal measurements of 3 m diameter, 8 m length and 63 $m^{-3}$ empty volume.

### 2.2. Sampling
Samples for metal analysis or toxicity testing were taken from the dust collected on a filter in the local extraction system which had a nominal pore size of 30 μm. The sample collected, therefore, represented all the dust present in the chamber atmosphere and not just welding fume. To provide a sample for online monitoring of atmospheric dust particle size, a penetration in the chamber hull was plumbed with a quarter turn valve on the outside of the chamber which was adjusted to give a free flow at atmospheric pressure of 27 litre minute-1 into an open ended 2m length of 19 mm diameter tungum pipe. Inside the chamber, the gas inlet for the sample line was at waist level and sampled the general chamber atmosphere. The length of pipe descended on the outside of the chamber and

allowed gas sampling from it into the analysers. The analyser sample tubes were inserted into the open end of the tungum pipe. Sampling was therefore performed at one atmosphere pressure.

### 2.3. Metal analysis and toxicity tests

Metal analysis was carried on dust samples from three welding trials. The dust was digested on a hotplate in a one to five mixture of nitric acid in hydrogen peroxide. Analysis in duplicate was by inductively coupled mass spectrometry (Agilent 7500c) using an internal standard of 10 ppb rhodium. A full set of calibration and quantification of most elements was carried out with additional use of quality control certified reference material.

Silica analysis was carried out on the dust from two welding trials at the commercial laboratories in the Institute of Occupational Medicine, Edinburgh. Portions of the samples were finely ground to create particles of uniform size. These were scanned qualitatively using routine inductively coupled mass spectrometry. The resultant diffraction patterns were then compared with standard reference materials and search match indices.

The oxidative potential of dust samples from four welding trials was assessed by their capacity to deplete (oxidatively consume) the low-molecular weight respiratory tract lining fluid antioxidants ascorbate, glutathione and urate from a synthetic respiratory tract lining fluid at a range of particle concentrations. Samples were suspended in ultra pure (18$\Omega$) Chelex-resin treated water (pH adjusted to 7.0 with Chelex treated 1M HCl) at concentrations of 27.78, 55.56 and 111.11$\mu$g/ml. Samples were then vortexed for 10 minutes followed by 30 seconds of sonication on ice at an amplitude of 15 microns to produce an homogenous suspension. Control residual oil fly ash (ROFA – oxidatively active control) and carbon black (M120 – oxidatively inactive control) particulate samples were prepared in an identical fashion at a concentration of 55.56$\mu$g/ml. The oxidative activity of these suspensions was assessed using a synthetic respiratory tract lining fluid (RTLF) containing the antioxidants ascorbate (AA), urate (UA) and glutathione (GSH), each at 200$\mu$M. PM suspensions were added to achieve a final particle concentration of 25, 50 and 100$\mu$g/ml. Samples were then incubated for 4 hours at 37°C at which time the samples were acidified to stop oxidation reactions. Particles were then removed by centrifugation and the resultant supernatants assessed for remaining concentrations of ascorbate, urate by HPLC [4]. Glutathione was detected using a spectrophotometric method [5], which allows the simultaneous detection of oxidised (GSSG), total (GSx) and reduced (GSH) glutathione. For comparison, residual oil fly ash (ROFA) and inert carbon black (M120) were used as positive and negative controls respectively. Parallel control incubations were also carried out in the absence of dust with samples taken at 0 and at 4 hours to determine background rates of auto-oxidation.

Cytotoxity testing and assessment of inflammatory potential were carried out on dust samples from four separate welding trials. Nimrod c276 welding fume and DQ12 quartz c were also included in all experiments as control particles: At 24hrs post-exposure, cytotoxicity was measured by lactate dehydrogenase (LDH) release and inflammatory potential by the cells' ability to produce the pro-inflammatory cytokine interleukin 8 (IL-8). A549 Type II lung epithelial cells, were seeded into 24-well plates at a concentration of 71,250 cells/well in cell culture media containing 10% foetal calf serum (FCS) and cultured over-night. The following day, the cell culture media was removed, cells washed with phosphate buffered saline (PBS) and cultured for a further 24hrs in cell culture media containing 2% FCS. Cells were then treated for a further 24 hrs with the various particle types, at the various treatment doses, suspended in fresh 25 FCS cell culture media. Following the different cell treatments, the tissue culture plate were centrifuged at 250xg, for 10 minutes and the supernatants removed for LDH and IL-8 quantification. LDH was measured using a standard Roche LDH Cytotoxicity Assay. IL-8 was measured using a standard R&D IL-8 ELISA kit.

### 2.4. Welding fume particle size assessment

Particle size measurement was carried out during a single welding shift when the local extraction ventilation was described as ineffective by the welding team who were performing manual arc welding. The welders were wearing positive pressure respirators. A MSP Corporation Wide Spectrum Particle Spectrometer 1000XP was used to quantify particles of 10 to 200 nm in diameter.

The measurement was expressed as total particles ml$^{-1}$ and also in 47 grades of diameter. Particle concentration was also measured using a TSI Inc. P-Trak Model 8525 Ultrafine Particle Counter. Values were corrected for the effects of decompression by multiplication by chamber pressure in atmospheres absolute. Concurrent events in the chamber were taken from the welding log compiled by the welding supervisor who worked in close communication with the welders who were also monitored on closed circuit television.

## 3. Results

### 3.1. Metal and silica analyses

The metal analysis is summarised in table 2. Although calcium is the predominant element this measurement would have been subject to interference from the presence of titanium in the sample and is an overestimation. Nevertheless, calcium is a major constituent of welding rod coatings and high levels were expected. Period four transition metals were next best represented. Seven transition elements out of the ten in this period are in the table. The remaining three, scandium, vanadium and cobalt, however, were also detected although at levels marginally below the table cut point. Zirconium was detected and the source of this was almost certainly the grinding wheels used to shape the weld. Quartz and cristabolite levels were below the method's detection limits of 0.3% in both samples tested.

**Table 2.** Summary of Metal Analyses.

Units are μg g$^{-1}$ of sample and are expressed as the mean of the measurements made. Only elements present at >1μg g$^{-1}$ in all three samples are tabulated. Elements are in periodic table categories and transition metals are ordered by period.

| Element category | Element | WF002 | WF003 | WF006 |
|---|---|---|---|---|
| Alkali metals | Lithium | 50 | 72 | 660 |
| Alkali earth metals | Magnesium | 348 | 362 | 329 |
| | Calcium[a] | 8,558 | 26,913 | 21,058 |
| | Barium | 2.0 | 16 | 10 |
| Period 4 transition metals | Titanium | 100 | 330 | 290 |
| | Chromium | 2.2 | 4.9 | 4.2 |
| | Manganese | 460 | 746 | 663 |
| | Iron | 1,656 | 6,331 | 4,581 |
| | Nickel | 10 | 19 | 27 |
| | Copper | 1.4 | 4.6 | 3.6 |
| | Zinc | 13 | 22 | 11 |
| Period 5 transition metal | Zirconium | 54 | 205 | 151 |
| | Molybdenum | 1.4 | 4.2 | 2.7 |
| Other metals | Aluminium | 70 | 154 | 107 |
| | Lead | 1.4 | 1.5 | 1.5 |
| | Bismuth | 2.0 | 1.8 | 2. |
| Metalloids | Boron | 8.0 | 17 | 10 |
| | Silicon | 63 | 98 | 110 |

[a] The values for calcium are not corrected for titanium interference in the method of analysis used.

### 3.2. Oxidant potential assessment

The dust elicited significant and dose dependent losses of ascorbate (P<0.05) compared with background oxidation associated with the particle free controls after the 4hr exposure (figure 1). At the lowest dose of 25μg/ml the addition of all 4 particles led to a loss of ascorbate from the system. At the 50μg/ml particle concentration all 4 WPM samples were less reactive than ROFA, whilst

significantly more reactive than M120. Dose responses were seen with four of the particle samples with the exception of WPM003.
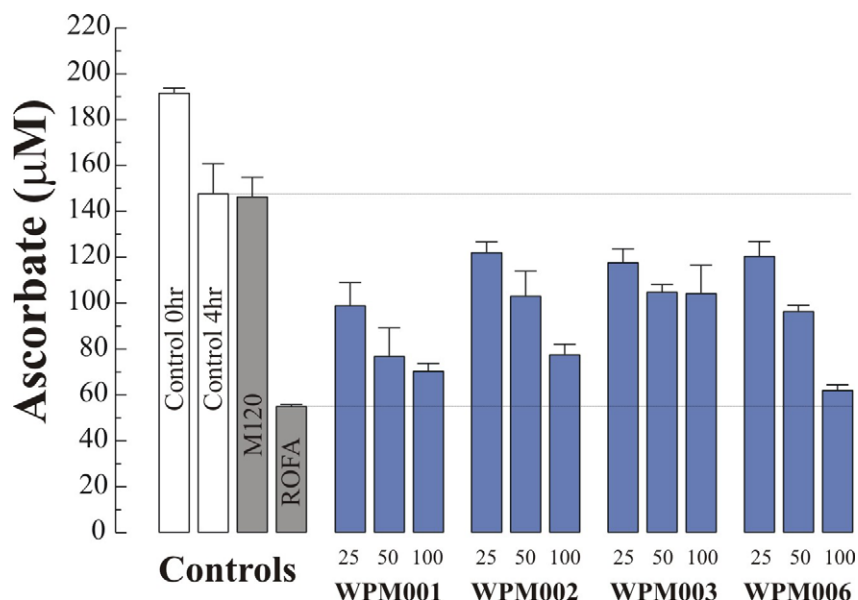


**Figure 1.** Ascorbate remaining in the synthetic RTLF after a 4-hour incubation with 25, 50 and 100µg/ml of WPM (blue bars). Control values are also displayed; particle-free controls at 0 and 4 hrs (white bars) and M120 and ROFA (grey bars) at 50µg/ml. Data are illustrated as mean (SD) of 3 separate experiments. WPM001-006 are the same samples as WF001-006.

All dust samples were less reactive towards glutathione with only sample 6 at the highest dose of 100µg/ml depleting significantly more GSH (-37.31µM) after the 4hr exposure than the particle free control. The loss in GSH observed with sample 6 was due to its oxidation to GSSG and did not reflect adsorption to the particle surface as no significant change was seen with total GSx concentrations. No depletion of urate was noted under any incubation condition.

3.3. Cytotoxicity and inflammatory potential assessment

After 24 hours exposure of A549 cells to welding fume at doses up to 500 µg ml$^{-1}$ there was little indication of cytotoxicity. In contrast, cytotoxicity rose rapidly with dose for Nimrod welding fume and DQ12 and, at 250 µg ml$^{-1}$ averaged 15% for each of the two agents.

IL-8 release in the untreated preparation was 370 pg ml$^{-1}$. At lower doses of fume, hyperbaric welding fume had significant effects (figure 2). The four hyperbaric welding fume samples induced a higher IL-8 response than the control particles but this result then reversed as the dose increased with the toxic control particles (DQ12 and Nimrod) becoming more active than the welding fumes. Increased activity was sustained up the full dose of fume for DQ12 but, at doses of more than 150 µg ml$^{-1}$ Nimrod fume was inhibitory. At a dose of 250 µg ml$^{-1}$ IL-8 release was significantly suppressed by Nimrod welding fume at a mean level of 187 pg ml$^{-1}$ and stimulated by DQ at a mean level of 723 pg ml$^{-1}$ while it was essentially no different to the untreated control for the hyperbaric welding fume samples.
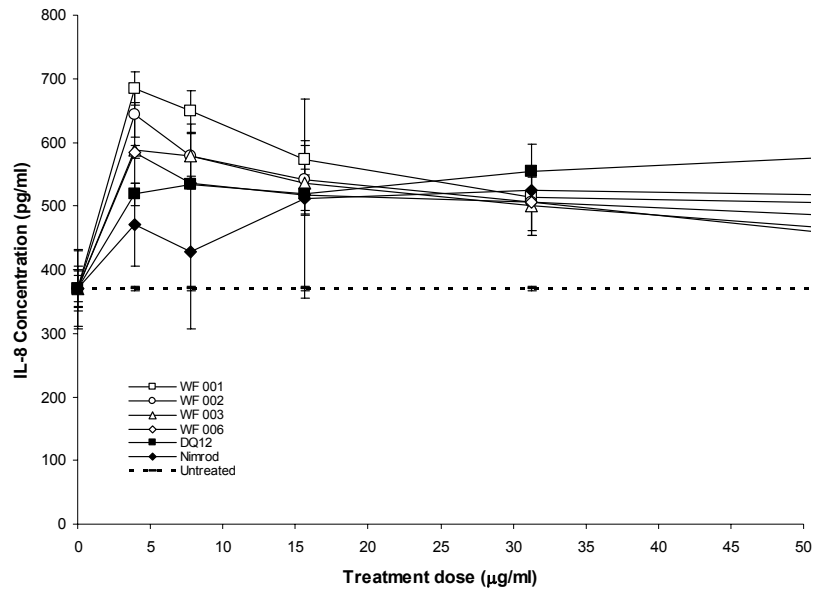
**Figure 2.** IL-8 Release 24 hours after exposure with treatment dose 0-50 μg ml$^{-1}$

## 3.4. Welding fume particle size assessment

Data gathered by the WPS during a welding session are shown in figure 3. It is clear that the fume is largely nanoparticulate in nature. Total values of particles from the same welding session are shown in figure 4 as measured by both the WPS and P-Trak. The P-Trak substantially underestimated particle concentration while welding was being performed. The overall distribution of particle size during the welding session is shown in figure 5. Over the period monitored, mean particle diameter was 29 nm (sd 17 nm) with a distribution mode of 22 nm. From the distribution plot it seems probable that there is a substantial amount of fume of a diameter less than 10 nm.

## 4. Discussion

Hyperbaric welding fume, while not being demonstrably cytotoxic in this study does have the potential to cause oxidative stress and induce inflammation at relatively low levels. This may be attributable to the representation of transition metals in the fume. Such metals are oxidatively active and have been associated with the inflammatory effect of other types of welding fume [6]. Under the conditions encountered by hyperbaric welders this gives some cause for concern as they breath a raised partial pressure of oxygen of 30-40 kPa for the duration of their work at pressure. An active hyperbaric welder may spend 90-150 days at pressure in any one year. Under such conditions any oxidative stress may be amplified and this justifies further consideration and investigation.

11.0 - On Agas start to weld
12.50 - Off Agas atmosphere good
12.50 - Divers leave work chamber
13.00 - Divers in work chamber
13.06 - Start welding
15.25 - Stop welding 10 passes completed
15.42 - Off Agas atmosphere good
15.58 - Divers leave work chamber
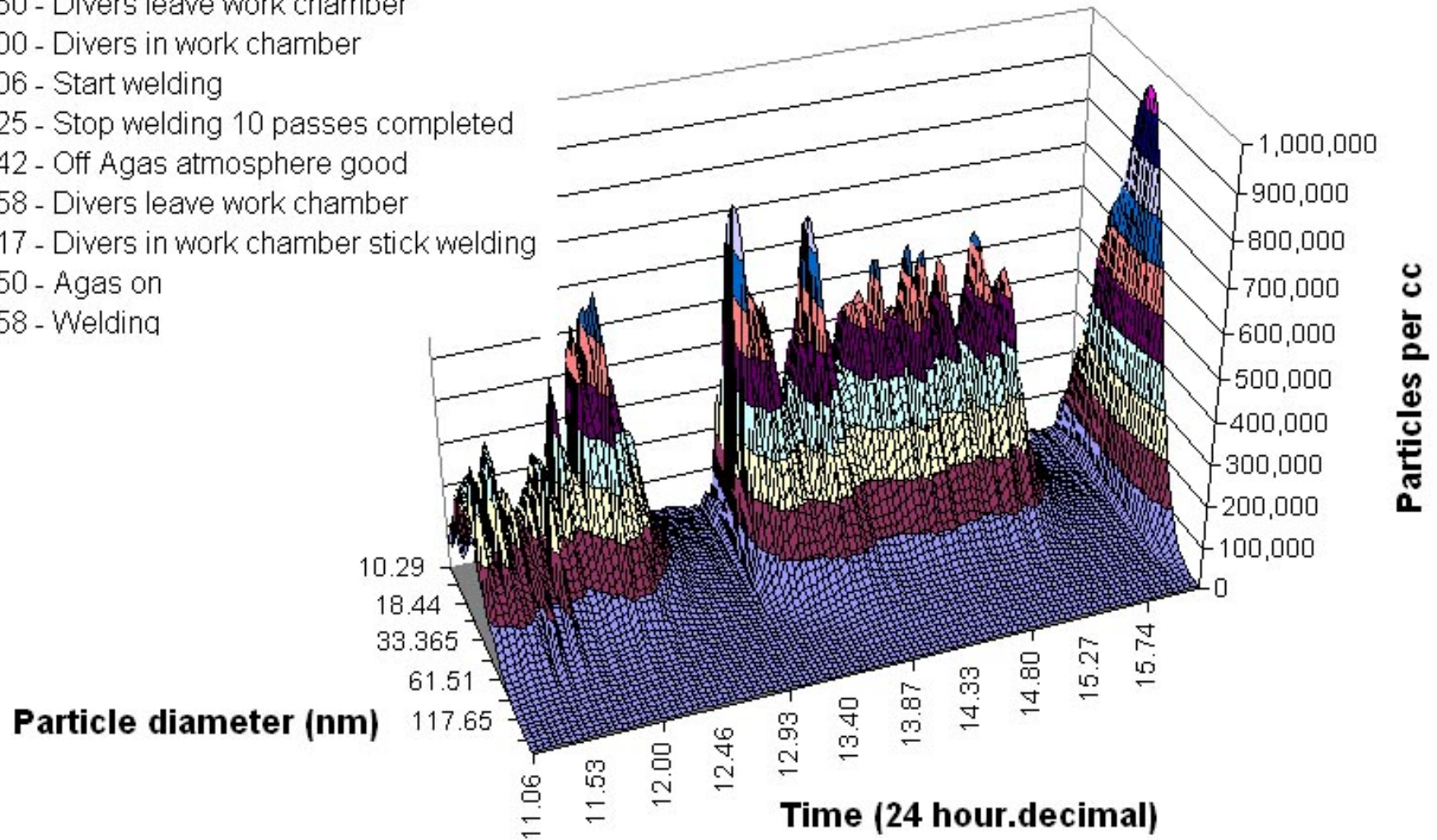16.17 - Divers in work chamber stick welding
16.50 - Agas on
16.58 - Welding

**Figure 3**. Three dimensional plot of WPS data during manual arc welding with indication of background events
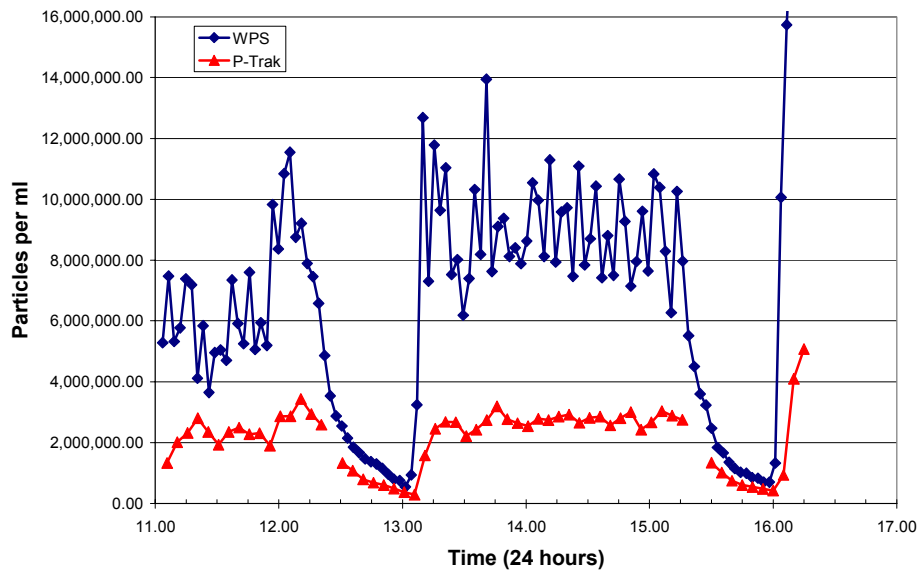
**Figure 4.** Total particle count over the same period as in figure 2 measured by both the WPS and P-Trak.
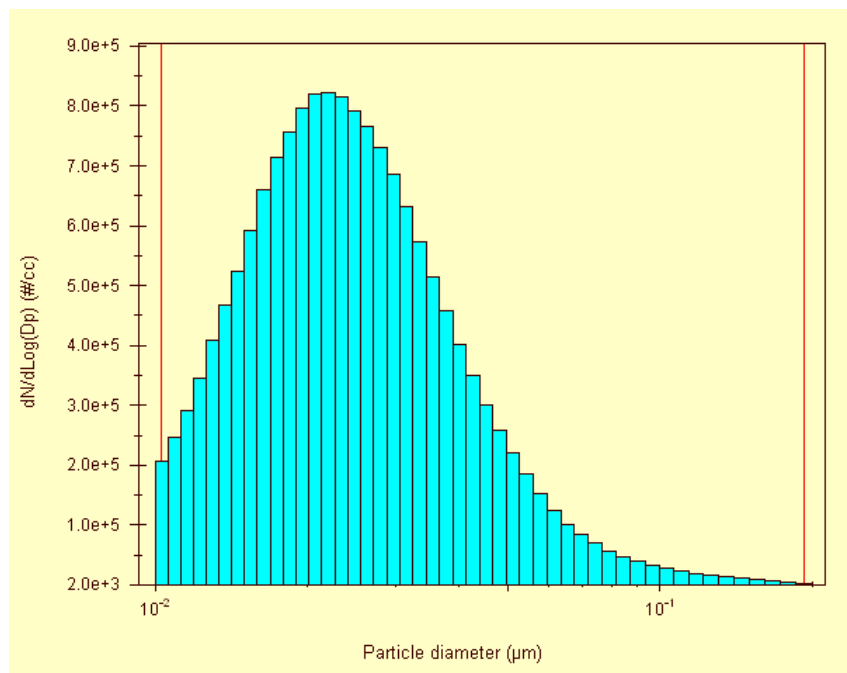


**Figure 5**. The average distribution of 110 samples analysed during the welding session from figure 2.

The particle diameter identified for hyperbaric welding fume was very low in this study. The fume generated by welding which employs flux contain a mixture of chainlike and spherical structures which suggest that condensation of vapour into primary particles and this is followed by a complex and dynamic process which includes coagulation, condensation and oxidation [7]. Agglomeration of particles occurs and it is assumed that this occurs before the fume reaches the welder's breathing zone and there is work to support this for $CO_2$ arc welding [8]. This assumption regarding agglomeration is

carried into the specification for particle respirators for use during welding which work to a particle size of 300 nm and above. At first sight this would seem to be an unjustified assumption for hyperbaric welding. There are factors that may influence the fume generated in hyperbaric welding. The atmosphere is largely composed of helium and contains a low concentration of oxygen. Vapour condensation may be affected as the thermal properties of helium produce higher cooling rates and there may be less oxidation of the fume constituents. The observation of a high concentration of nanoparticles in this study does not preclude the presence of larger agglomerated particles since these were not studied. The presence of such small particles, however, does give rise to some cause for concern. The filter respirators used by welders are not tested against such dust and as particle diameter falls there is a greater chance of inward leakage round the edge of any face mask so reducing the protection offered.

The mean particle diameter identified was 29 nm. At this diameter, approximately 80% of fume is retained in the lung with 40% being deposited in the alveolar region. Unagglomerated ultrafine particles are not phagocytosed efficiently by macrophages and this can lead to a major accumulation of particles if exposure is continued and ultrafine particles can pass through the epithelium to the interstitial tissues. At lower particle size increasing fractions of particles are deposited in the extrathoracic and tracheobronchial airways. The effects of such ultrafine dusts have recently been comprehensively reviewed [9]. Such low particle sizes are difficult to assess by simple online analysis and this is demonstrated here by the performance of the P-Trak analyser which measures form 20 nm in contrast to the WPS unit which measures from 10 nm. A small difference in capability lead to a very large discrepancy in measurement. With adequate characterisation of the fume of a particular operation, however, it may be possible to introduce correcting factors so that any risk is not overlooked. Online analysis to assess risk with such small particles seems appropriate since at quite high concentrations there may be no perception of a hazard in the immediate environment and welders in this study felt able to remove respiratory protection at particle levels of 1,000,000-2,000,000 particles ml$^{-1}$ (figures 3 and 4)

This study has weakness and strengths. Particle sizes greater than 200 nm were not studied in detail and so the presence of larger agglomerated particles was not identified. Also such particles may be held together by weak attracting forces which might have been sheered apart in the orifice of the quarter turn valve controlling sample flow from the chamber. This effect would lead to a lowering of observed particle size. This point remains to be addressed by the use of a laminar flow sampling system. It is tempting to assume that the fume observed during welding operations is entirely fume coming from the welding process itself. Grinding, however, is an important process in the type of weld monitored in this project and the welders here were used high speed grinders as much as welding torches. This is reflected by the finding of zirconium in the metal analysis. The study examined, therefore, fume and dust from combined welding and grinding operations and not just welding alone. Strengths of the study lie in the ability to observe welding operations at increased ambient pressure. For analysis, the sample was decompressed and, consequently diluted due to expansion during decompression. This gives the ability to observe higher concentration of particles by on-line analysis than is possible at atmospheric pressure. For example the P-Trak has a measurement range of 0-500,000 particles ml$^{-1}$ and in this study was used to identify particle concentrations of up to 5,000,000 particles ml$^{-1}$.

In conclusion, this study has identified the predominance of nanoparticulate as a result of hyperbaric welding operations. The fume has the potential at relatively low concentrations to cause oxidant stress and inflammation and these properties have the potential to interact with other factors in the hyperbaric diving environment.

**References**
[1]    Racette BA, McGee-Minnich L, Moerlein SM, Mink JW, Videen TO and PerlmutterJS 2001 Welding-related parkinsonism: clinical features, treatment, and pathophysiology Neurology **56** 8-13.

[2]     Palmer KT, Poole J, Ayres JG, Mann J, Burge PS and Coggon D **E**xposure to metal fume and *infectious pneumonia* Am. J. Epidemiology. **157** 227-33

[3]     Sjogren B, Gyntelberg F and Hilt B. *Ischemic heart disease and welding in Scandinavian studies* Scand. J. Work, Environ. Health **Suppl 2** 50-3

[4]     Macdiarmid JI, Ross JAS, Taylor CL, Watt SJ, Adie W, Osman LM, Adie W, Godden D, Murray AD, Crawford JR and Lawson A 2004 *Co-ordinated investigation into the possible long term health effects of diving at work. Examination of the long term health impact of diving*. Research Report 230. (Sudbury: HSE Books)

[5]     Baker MA, Cerniglia GJ, and Zaman A 1990.*Microtiter plate assay for the measurement of glutathione and glutathione disulfide in large numbers of biological samples* Anal Biochem **190** 360-5

[6]     Mudway IS, Stenfors N, Duggan ST, Roxborough H, Zielinski H, Marklund SL, Blomberg A, Frew AJ, Sandstrom T, Kelly F 2004 A*n in vitro and in vivo investigation of the effects of diesel exhaust on human airway lining fluid antioxidants* Arch Biochem Biophys **423** 200-12

[7]     McNeilly JD, Heal MR, Beverland IJ, Howe A, Gibson M.D, Hibbs LR, MacNee W, Donaldson K 2004. *Soluble transition metals cause the pro-inflammatory effects of welding fumesin vitro* Toxicol. Appl. Pharmacol. **196** 95–107

[8]     Zimmer AT 2002 *The influence of metallurgy on the formation of welding aerosols* J. Environ. Monit. **4** 628-632

[9]     Saito H, Ojima J, Takaya M, Iwasaki T, Hisanaga N, Tanaka S and Arito H 2000 *Laboratory measurement of hazardous fumes and gases at a point corresponding to breathing zone of welder during $CO_2$ arc welding* Ind. Health **38** 69-78

[10]   Ostiguy C, Lapointe G, Trottier M, Menard L, Cloutier Y, Boutin M, Antoun M and Normand C 2006 *Health effects of nanoparticles* (Montreal: IRSST – Communications Division)