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**Final report on JS2002837
Measurement of HCl in workplace air**

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FOREWORD

A review of hydrogen chloride carried out in the late 1990s by the Health and Safety Executive (HSE) working group on the assessment of toxic chemicals (WATCH) drew attention to the difficulty of measuring exposure to hydrogen chloride and hydrochloric acid mist (HCl). This problem was underlined by concern expressed by the Galvanizers Association about the lack of methods suitable for measurement of HCl in their industry. In response to this situation, HSE decided that a project should be funded to develop and validate a method for HCl that could be considered for publication in its Methods for Determination of Hazardous Substances (MDHS) series. Accordingly, when the Engineering & Utilities Sector of HSE's Field Operations Division issued Sector Information Minute SIM 03/1999/13 in 1999, it contained the statement: "The Health and Safety Laboratory (HSL) are currently developing alternative techniques for the monitoring of HCl in workplace air. These are currently at an early stage, but may progress to field trials if promising results are obtained." However, this commitment to develop an effective solution to the problem of measuring exposure to HCl was not followed up until 2002, when the support job that forms the subject of this report, JS2002837, was commissioned to enable the necessary work to be carried out.

CONTENTS

1	INTRODUCTION	1
2	OBJECTIVES	2
3	WORK PROGRAMME	3
3.1	Overall strategy.....	3
3.2	Job plan	3
4	REVIEW OF PUBLISHED METHODS	5
4.1	Preliminary consideration of the particle size collection characteristics of the sampler.....	5
4.2	Sorbent tube method	5
4.3	Filter and sorbent tube method.....	5
4.4	Two-stage filter method	6
4.5	Radiello diffusive samplers	6
5	IMPLICATIONS OF THE USE OF PUBLISHED METHODS	7
5.1	HCl collection efficiency	7
5.2	Possible reaction of HCl with co-sampled particulate matter	7
5.3	Possible reaction of sulphuric acid mist with co-sampled chloride-containing particulate matter.....	7
5.4	Particular problems of relevance to the galvanizing industry	7
5.5	Potential use of denuders	8
5.6	Sampling of related inorganic gases.....	9
6	EXTERNAL CONSULTATION	10
6.1	Liaison with ISO/TC 146/SC 2/WG 2	10
6.2	Collaboration with the Galvanizers Association	10
7	LABORATORY TESTS	11
7.1	Filter blank levels	11
7.2	HCl collection efficiency	11
7.3	Influence of co-sampled particulate matter	12
7.4	Ammonium chloride collection efficiency	14
8	METHOD SELECTION.....	16
9	FIELD SAMPLING VISITS TO UK GALVANIZERS	17
9.1	Purpose	17
9.2	Hot dip galvanizing	17
9.3	Substances to which galvanizing workers are potentially exposed.....	19
9.4	Work patterns	19
9.5	Sampling and analysis.....	20
9.6	Results and discussion	20
10	CONCLUSIONS	23

11	APPENDICES	24
	APPENDIX A — PERSONAL EXPOSURE MEASUREMENTS: RESULTS SUMMARIES, SITE BY SITE.....	25
	APPENDIX B — PERSONAL EXPOSURE MEASUREMENTS: OVERALL RESULTS SUMMARY	30
	APPENDIX C — SUMMARY OF FIXED-POINT (STATIC) MEASUREMENTS NEAR PICKLING BATHS.....	31
	APPENDIX D — COMPARISON OF SILICA GEL TUBES AND RADIELLO DIFFUSIVE SAMPLERS WITH THE PERFORMANCE OF THE TWO-STAGE FILTER SAMPLING METHOD	32
	APPENDIX E — COMPARISON WITH PREVIOUSLY PUBLISHED DATA...	33
12	REFERENCES	34

EXECUTIVE SUMMARY

Objectives

The objectives of the work were to develop a method for measurement of HCl in workplace air that would be suitable for publication in HSE's Methods for Determination of Hazardous Substances (MDHS) series; and then to carry out field trials in galvanizing works to determine the performance of the method and provide exposure data for HSE's National Exposure Data Base (NEDB) that are suitable for use in assessing the performance of the EASE (Estimation and Assessment of Substance Exposure) model when applied to soluble gases.

Main Findings

A review of available methods for measurement of HCl and other chemical agents to which workers in the galvanizing industry are exposed revealed a number of areas of potential concern with existing published methods. The most important of these issues were investigated and it was concluded that the best method for sampling HCl and other chemical agents to which workers in the galvanizing industry are exposed is a two-stage filter method, using a GLA-5000 PVC prefilter to collect ZnCl₂, ZnO and NH₄Cl and a sodium carbonate-impregnated QMA quartz fibre filter to trap HCl.

Field sampling visits were carried out at nine galvanizing plants and these generated a considerable volume of exposure data for NEDB. Picklers were found to experience the highest exposure to HCl, whilst galvanizers had the highest exposures to ZnCl₂, ZnO and NH₄Cl. The median values of the exposures concerned were 0.55 mg m⁻³, 0.44 mg m⁻³, 0.17 mg m⁻³ and 0.36 mg m⁻³, respectively, all of which are well below the relevant exposure limits of 1.5 mg m⁻³ for HCl (WEL), 1 mg m⁻³ for ZnCl₂ (WEL), 5 mg m⁻³ for ZnO (former OES) and 10 mg m⁻³ for NH₄Cl (WEL). However, maximum exposures measured for HCl (2.22 mg m⁻³) and ZnCl₂ (1.84 mg m⁻³) were above the WELs and there is therefore scope for improvement in control measures. The exposure data arising from the field visits (nearly 400 results) have been added to NEDB, along with summary reports for each of the galvanizing plants visited.

The field sampling visits also provided an indication of how the performance of the sorbent tube and two-stage filter methods for HCl compare. The scatter of paired results was very wide, as might be anticipated for a field comparison of measurement methods, but on average silica gel tubes were found to collect around 85% of the HCl sampled using the two-stage filter method. This was as expected, since the particle size collection characteristics of silica gel tubes do not match the inhalable convention and they will therefore tend to under sample HCl mist and particulate chlorides. Radiello diffusive samplers were found to over sample in comparison to the two-stage filter method, but it seems likely that this was due to contamination of the external diffusive body of the samplers, which appears to be drawback of this type of device.

Recommendations

Further work is required to determine the performance characteristics of available methods before a definitive recommendation for a method for HCl measurement can be made. A collaborative sampling exercise has therefore been organised to determine the performance characteristics of filter, sorbent tube and Radiello diffusive sampler methods for measurement of HCl. This exercise, which is scheduled to take place from 14-17 February 2006 at the Berufsgenossenschaftliches Institut für Arbeitssicherheit (BGIA) test gas facility in Sankt Augustin, will be carried out under support job JS2003532, the 'Inorganic substances-in-air work programme'. It will also investigate further the extent of potential interferences in HCl exposure measurement caused by reaction of HCl with co-sampled particulate matter.

1 INTRODUCTION

A number of methods have been published for the measurement of hydrogen chloride (HCl) in workplace air, most notably by the United States National Institute of Occupational Safety and Health (NIOSH) [1], the Deutsche Forschungsgemeinschaft (DFG) [2] and the Institut National de Recherche et de Sécurité (INRS) [3]. However, none of the published methods adequately addresses the problems that can occur when sampling HCl in galvanizing workshops, where there is mixed exposure to HCl and other chloride-containing chemicals, e.g. zinc chloride (ZnCl_2) and ammonium chloride (NH_4Cl), and potential interference from substances that react with HCl, e.g. iron, iron oxide (Fe_2O_3) and zinc oxide (ZnO). Hence, there has been concern about the reliability of exposure data for HCl, including that contained in HSE's National Exposure Data Base (NEDB), much of which will probably have been obtained using the NIOSH method [1].

2 OBJECTIVES

The objectives of the work were to develop a method for measurement of HCl in workplace air that would be suitable for publication in HSE's Methods for Determination of Hazardous Substances (MDHS) series; and then to carry out field trials in galvanizing works to determine the performance of the method and provide exposure data for NEDB that is suitable for use in assessing the performance of the EASE (Estimation and Assessment of Substance Exposure) model when applied to soluble gases.

3 WORK PROGRAMME

3.1 OVERALL STRATEGY

The overall strategy for the work was to begin by undertaking a review of published methods for measuring exposure to hydrochloric acid and considering potential alternative approaches. A preferred method would then be established and validated in laboratory experiments. This would be followed by field trials, which would have the dual purpose of evaluating the performance of the method in different work environments, in particular in galvanizing works, and also providing exposure data for NEDB. It was decided that the scope of the field trials would be determined after consultation with the customer, taking into account the applicability of the method developed and the available resources.

3.2 JOB PLAN

3.2.1 Original job plan

The original job plan was as follows:

- 1) Review published methods for measurement of volatile inorganic acids in workplace air, in particular HCl.
- 2) Consider the implications of the use of published methods for sampling HCl, in particular in the galvanizing industry, and decide what aspects of the methodology need to be examined in the laboratory.
- 3) Discuss methods for measurement of volatile inorganic acids in workplace air with experts from ISO/TC 146/SC 2/WG 2, with a view to identifying methodology which could be suitable for incorporation in a future MDHS and which is compatible with the methodology that will feature in the proposed International Standard on determination of inorganic acids in workplace air.
- 4) Arrange a meeting with the Galvanizers Association to discuss the planned work and, in particular, seek agreement for co-operation of members of the Galvanizers Association in field evaluation of the proposed method after its evaluation in the laboratory.
- 5) Carry out laboratory tests to examine aspects of the methodology that were identified for further investigation in (2) and select a method for further evaluation and use in field trials.
- 6) Evaluate the performance of the method to demonstrate that it complies with the requirements of BS EN 482 [4] and determine the uncertainty of the method according to the ISO GUM [6].
- 7) Carry out field trials in galvanizing works to determine the performance of the method for measurement of HCl and provide exposure data for NEDB.

3.2.2 Modified job plan

The job plan was modified before work started after the customer requested a shift in emphasis away from method development and validation and towards collection of exposure data for NEDB. It was agreed that laboratory work would be restricted to the minimum required to establish a working method and that remaining resources would then be devoted to field visits to collect data on HCl exposure in the galvanizing industry. Laboratory work to obtain further method validation would be carried out under support job JS2003532, the 'Inorganic substances-in-air work programme'. Hence, work carried out under item 5 of the above job plan was curtailed and item 6 was dropped altogether.

4 REVIEW OF PUBLISHED METHODS

4.1 PRELIMINARY CONSIDERATION OF THE PARTICLE SIZE COLLECTION CHARACTERISTICS OF THE SAMPLER

The workplace exposure limit (WEL) for HCl published in EH 40 [7] applies to equally to hydrochloric acid mist and hydrogen chloride gas, both of which can be present in workplace air. It is therefore important that the sampling method used collects both of these forms of HCl and that the particle size collection characteristics of the sampler match the inhalable convention, as defined in BS EN 481 [8].

4.2 SORBENT TUBE METHOD

NIOSH Method 7903 [1] describes a method for determination of inorganic acids (including the volatile acids HF, HCl, HBr and HNO₃) in workplace air. This method involves sample collection using a sorbent tube containing washed silica gel and analysis by ion chromatography (IC). It has been widely used in the UK for many years, but it has a significant drawback, insofar as the particle size collection characteristics of the sorbent tube have been shown [9] not to match the inhalable convention. This could lead to significant under-sampling of hydrochloric acid mist in some situations. There is also the potential of interference from chloride-containing particulate matter, although NIOSH suggest that the resulting over-estimation of volatile acid gases, including HCl, can be avoided by discarding the glass fibre plug and filter that are used to retain the silica gel in the tube. This needs investigation, however, as if sampled HCl is partly trapped on the glass fibre there could be a loss of sample if the plug and filter are discarded.

4.3 FILTER AND SORBENT TUBE METHOD

A method similar to that described by NIOSH has been developed in Germany by the Berufsgenossenschaftliches Institut für Arbeitssicherheit (BGIA). This uses a sampling train consisting of a PTFE filter and silica gel sorbent tube connected in series. The filter is designed to remove any interfering chloride-containing particulate matter and transiently collect hydrochloric acid mist. The hydrochloric acid mist does not remain on the filter but rapidly evaporates and is collected, along with any HCl that was initially present in the sampled air in the gaseous phase, on the silica gel sorbent tube. An English version of the BGIA method is included as a DFG method in a book published by Wiley [2].

However, the German approach suffers from problems similar to those that occur with the NIOSH method [1]. The main concern is that the sorbent tubes are used at a flow rate of 200 ml/min and this sampling rate is not compatible with the use of samplers that collect the inhalable fraction of airborne particles, which is the particle size range of interest in the case of hydrochloric acid mist. For example, an IOM sampler is used at 2 l/min and a standard German GSP sampler is used at 3.5 l/min.

Current practice in Germany seems to be to ignore the particle size collection characteristics of the filter sampler. This is possibly due to a misconception that because the hydrochloric acid mist ends up on the sorbent tube, the aerosol collection characteristics of the sampler are unimportant. The matter has been raised recently with BGIA and they appear to recognise that it is something that might need to be reconsidered. However, for the time being, BGIA continues to use a sampling train comprising of a sorbent tube preceded by a Millipore sampling cassette, the particle collection characteristics of which do not match the inhalable convention. With this arrangement there is a significant risk of under-collection of hydrochloric acid mist.

BGIA have in fact already developed two samplers that potentially get around this problem, but neither is used at present. Both are modified GSP samplers that are commercially available in Germany. The GGP sampler uses a back-up sorbent cartridge that is loaded and unloaded in the laboratory. It is used widely in Germany for sampling substances that are present in the air in both gaseous and particulate states, so-called mixed-phase aerosols, such as metalworking fluid aerosols generated from low volatility mineral oils. It could also be used for sampling HCl, but it is likely that there would be a blank problem due to the relatively large amount of washed silica gel that would be required as sorbent. The other sampler that could be used for HCl is the GGP-U sampler, which uses three back-up sorbent tubes mounted in parallel in a specially designed holder, together with a GSP sampler fitted with one of a series of non-standard sampling cones designed to collect the inhalable fraction of airborne particles at flow rates lower than the standard 3.5 l/min. The main disadvantage with this arrangement is one of cost, not only that of the sampling device but also because three sorbent tubes are required to collect a single air sample.

4.4 TWO-STAGE FILTER METHOD

INRS have published Métropol Fiche 009 [3] on the determination of inorganic acids in workplace air, including HCl. A PVC or PTFE membrane filter is used to collect the acid mist and other particulate material, allowing the gaseous phase to pass through and be collected on a quartz fibre filter that has been impregnated with sodium carbonate solution.

The INRS approach has the potential for considerable improvement on the BGIA and NIOSH methods, as it should be possible to use a two-stage filter method to collect hydrochloric acid mist effectively. However, unfortunately the two-stage filter method, as it is used by INRS, has a problem, in that the membrane and sodium carbonate-impregnated quartz fibre filters used in the Métropol method are mounted in Millipore sampling cassettes and it has been shown [10] that these are not good at collecting the inhalable fraction of airborne particles. However, more recently, Demange *et al* [11] have attributed the perceived poor particle size selection characteristics of Millipore cassettes to the deposition of a significant proportion of the airborne particles that pass through the entry orifice on the internal surfaces of the sampler, rather than on the filter. They propose the use of sample dissolution within the cassette to get around this problem. However, this should be unnecessary for HCl because any hydrochloric acid mist depositing on the walls of the cassette should evaporate during sampling and be collected on the secondary sodium carbonate-impregnated quartz fibre filters. Therefore, if the findings of Demange *et al* are correct, and they are applicable in situations in which exposure to hydrochloric acid mist occurs, the Métropol method would seem to be entirely satisfactory for sampling HCl. If this is not the case, the two filters could alternatively be mounted in an IOM or GSP sampler.

4.5 RADIELLO DIFFUSIVE SAMPLERS

Radiello manufactures a diffusive sampler for HCl. This device determines hydrogen chloride gas and is primarily intended for sampling ambient air. It consists of an external diffusive body, into which is placed a collection cartridge containing washed silica gel tubes. A certified uptake rate for HCl is provided with the collection cartridges, but there is no published data on the performance of the device. Nevertheless, it was decided that its potential for workplace air sampling was worth considering in this work.

5 IMPLICATIONS OF THE USE OF PUBLISHED METHODS

5.1 HCL COLLECTION EFFICIENCY

The DFG [2] and INRS [3] methods both use a pre-filter to remove interfering chloride-containing particulates. They rely upon any hydrochloric acid mist collected on the pre-filter not remaining on it, but rapidly evaporating and passing down the sampling train to be collected, along with any HCl that was initially present in the sampled air in the gaseous phase, on a silica gel sorbent tube or sodium carbonate-impregnated quartz fibre filter. However, no published data could be found to support the contention that HCl is not retained on the pre-filter, so it was decided that this should be verified in the planned laboratory tests. Similarly, the INRS [3] method involves the use of sodium carbonate-impregnated quartz fibre filters to trap gaseous HCl, but it contains no information about the collection efficiency of the filters. Hence, it was decided that this should also be checked in the planned laboratory tests.

5.2 POSSIBLE REACTION OF HCL WITH CO-SAMPLED PARTICULATE MATTER

Something that may have been overlooked by those who have developed published methods is that hydrochloric acid mist might be expected to react with co-sampled particulate matter on pre-filters used to remove interfering chloride-containing material. For example, hydrochloric acid may react with metals or metal oxides that could be present in a galvanizing workshop, e.g. iron, iron oxide, zinc oxide etc. If this occurs it will lead to low results. It was therefore decided that the planned laboratory tests should established whether or not such interferences occur and, if so, the extent of the problem.

5.3 POSSIBLE REACTION OF SULPHURIC ACID MIST WITH CO-SAMPLED CHLORIDE-CONTAINING PARTICULATE MATTER

If sulphuric acid (H_2SO_4) is present as a mist in the sampled air, there is a theoretical possibility that it could displace HCl from co-sampled chloride-containing particulates. No report of this occurring has been found in the literature, so it would be instructive to perform laboratory tests to investigate this potential interference. This could be achieved by spiking H_2SO_4 onto pre-filters loaded with chloride, drawing air through them and determining whether HCl is released and trapped on a back-up sorbent tube or sodium carbonate-impregnated quartz fibre filter. However, due to the curtailment of the method validation work under the revised job plan, it was decided not to investigate this further under JS2002837. The reason for this is because the job is primarily concerned with the measurement of HCl in the UK galvanizing industry, in which parallel exposure to H_2SO_4 does not normally occur.

5.4 PARTICULAR PROBLEMS OF RELEVANCE TO THE GALVANIZING INDUSTRY

It is not practicable to directly determine the amount of HCl present in a workplace air sample by measuring its acidity. It is therefore necessary to calculate it after determining the amount of chloride in the sample that is attributable to the presence of HCl in the air. This task is complicated considerably when there are a number of chloride-containing species present in the air, as is the case in a galvanizing workshop.

Hydrochloric acid is used in the galvanizing industry as a 'pickling' agent, i.e. it is used to remove rust from the work piece. However, chloride is present in galvanizing workshop air in substances other than HCl. In particular, NH₄Cl is commonly used as a flux in the galvanizing process. The work piece is either coated with NH₄Cl before it is dipped into molten zinc or it is dipped into molten zinc through a layer of NH₄Cl. In both cases, NH₄Cl vapour is released into the workplace, along with ZnCl₂ fume generated in the galvanizing process as a result of reaction between NH₄Cl and molten zinc. In addition to these chloride-containing species, ZnO fume and ZnO dust are also found in the air of galvanizing workshops. It is therefore necessary to measure a number of different hazardous substances in the air a galvanizer breathes in order to obtain a comprehensive assessment his exposure by inhalation. This presents a challenge in both sampling and analysis. All the substances of interest have to be collected by the sampling method, the analytical method has to enable them to separately determined and the two parts of the measurement procedure have to be mutually compatible.

The use of a two-stage sampler, either a sorbent tube and pre-filter, as used in Germany [2], or an sodium carbonate-impregnated quartz fibre filter and pre-filter, as used in France [3], goes a long way to fulfilling the sampling requirements. The pre-filter removes non-volatile chloride-containing particulate matter allowing the HCl to pass through and be sampled on the second sampling medium. However, the presence of volatile NH₄Cl in galvanizing fume complicates the issue, because there is a possibility that this could pass through the pre-filter and be collected on the sodium carbonate-impregnated filter, leading to low NH₄Cl results and high HCl results. The extent to which this occurs was unknown and it was therefore decided that it should be investigated.

Analytical problems are a little more straightforward. A number of papers published a number of years ago [12], [13], [14] address the main issue of separately determining ZnCl₂, ZnO, NH₄Cl and HCl. As in more recent measurement procedures, these two groups of workers used a filter for sampling airborne particulates, but they used a now outdated impinger method for measuring HCl. The two groups employed slightly different analytical methods, but both relied upon the use of separate procedures to extract and then measure ZnO, ZnCl₂ and NH₄Cl on the filter. However, neither group considered the possibility of breakthrough of NH₄Cl, assuming that all the chloride in the impinger was associated with HCl; nor did they investigate the effectiveness of separating ZnCl₂ and ZnO on the basis of their widely different solubilities in water (432 g 100 cm⁻³ and 0.00016 g 100 cm⁻³ respectively). Although this warrants examination, due to the curtailment of the method validation work under the revised job plan, it was decided not to investigate this further under JS2002837, which is more concerned with HCl measurement.

5.5 POTENTIAL USE OF DENUDEERS

A denuder is a device that can be used to help characterise a mixed-phase aerosol such as hydrochloric acid mist. Denuders typically collect the gaseous phase by diffusion onto the sorbent-coated internal walls of the device. They are used in combination with a filter to collect the particulate phase that passes through the device and a back-up impregnated filter to collect vapour released from any volatile particulate material collected. When the three samples are analysed the result from the denuder yields the concentration of the substance present in the sampled air in the gaseous phase, whilst the sum of the results from the filter and back-up sorbent tube yields the concentration of the substance present as airborne particles. However, the results obtained may not give an accurate estimate of the distribution between the gaseous and particulate phases. This is because the gaseous phase is stripped out of the sampled air as it passes through the denuder and evaporation of the substance from the particulate phase will therefore occur to redress the balance. The extent to which this happens and hence the accuracy of the results depends upon the volatility of the substance concerned.

Denuders were first developed for use in ambient air sampling and most available devices are large and heavy. They come in various designs, the most common being the so-called annular denuder, in which the sampled air passes through a number of parallel tubes, often made of glass, onto the surface of which the sorbent coating is applied. Another design, which is considerable smaller, features a glass honeycomb. In recent years, smaller denuders have been developed for personal sampling, some of which are now commercially available [15], [16]. However, they are still quite bulky, designed for ambient air monitoring and relatively expensive.

The high volatility of HCl means that it is unlikely that any meaningful information about the relative concentrations of HCl mist and vapour can be obtained using a denuder, since all the HCl will probably be stripped out of the particulate phase as the sampled air passes through the device. Fortunately, despite the fact that hydrochloric acid mist is a mixed-phase aerosol, there is currently no need for separate measurement of HCl mist and vapour, since there is a single exposure limit covering both phases. Nevertheless, a denuder could still have some use for HCl because it could potentially be used to separate HCl from substances that are potential interferents when collected on a pre-filter (see 5.1 and 5.3). It would therefore be informative to carry out tests to investigate the potential use of denuders for HCl measurement. However, once again, due to the curtailment of the method validation work under the revised job plan, it was decided not to investigate this further under JS2002837.

5.6 SAMPLING OF RELATED INORGANIC GASES

The priority for the present work is to address the problem of measuring exposure to HCl in the galvanizing industry, in which it is unlikely that there will be exposure to other inorganic acids and related inorganic gases. However, in other workplaces such mixed exposure can occur.

Hence, it would be useful to consider the problem of sampling in situations where there is mixed exposure to HCl and other inorganic acids. Some of these acids (HF, HBr and HNO₃) are volatile and have sampling problems similar to those for HCl; others inorganic acids (H₃PO₄ and H₂SO₄) are non-volatile and need a slightly different sampling strategy. In particular, for non-volatile inorganic acids it is not possible to use a prefilter to remove interfering particulate matter and there is no need to alkali-treat the sampling filter.

Taking this one step further, it would also be useful to consider how to sample inorganic acids in situations where there could also be exposure to related inorganic gases such as NO₂, SO₂ etc. A method developed by the National Institute of Occupational Health (NIOH) in Norway uses a stack of three filters to sample inorganic acids and related inorganic gases: a front filter for collection of non-volatile acid mist, a second sodium carbonate-impregnated quartz fibre filter for collection of volatile acid vapours and SO₂ and a third sodium iodide/ethylene glycol-treated filter for collection of NO₂.

Ideally, a versatile method suitable for measurement of all inorganic acids and related gases would be developed and validated. However, this is outside the scope of the present work.

6 EXTERNAL CONSULTATION

6.1 LIAISON WITH ISO/TC 146/SC 2/WG 2

ISO/TC 146/SC 2/WG 2 met in Umeå, Sweden in February 2003. On the agenda was a proposal for a new work item to develop an International Standard entitled *Workplace air — Determination of inorganic acids*. It was agreed that this standard, which will be ISO 21438, should be published in three parts. Part 1 will address *Non-volatile acids (sulphuric acid and phosphoric acid)*, Part 2 will deal with *Volatile acids, except hydrofluoric acid (hydrochloric acid, hydrobromic acid and nitric acid)* and Part 3 will be concerned with *Hydrofluoric acid and particulate fluorides*. The problems of measuring volatile acids, including HCl, were discussed at length during the Umeå meeting. However a decision about the methodology to be included in the volatile acids standard, ISO 21438-2, was postponed to a later date, the working group deciding instead to focus its efforts on drafting the non-volatile acids standard, ISO 21438-1. Nevertheless, the working group gave a strong indication that it was likely to include all methods with acceptable performance in ISO 21438-2, i.e. the methodology prescribed in the standard is expected to include that described in the DFG and INRS methods (see 4.3 and 4.4).

It was therefore assumed that the method selected for evaluation and use in the present job would be compatible with ISO 21438-2, whatever the exact details of the method, since the intention was to base it either on the DFG method [2] or on the INRS method [3]. This has proved to be a correct assumption, since the preliminary working draft of the standard prepared in 2005 describes a sampling method using a pre-filter to remove interfering particulates and either a sorbent tube or an impregnated quartz fibre filter to collect volatile acids.

6.2 COLLABORATION WITH THE GALVANIZERS ASSOCIATION

The Galvanizers Association have, for many years, been keen to see progress made with the development of a validated method for measuring exposure to HCl in their industry. The matter was first discussed in a meeting held at HSL, Sheffield, on 18th January 1999, which was organised by Mr Cain (HSE) and attended by Mr Howe (HSL), Mr Piatkiewicz (Galvanizers Association), Mr Hill (Wedge Group Galvanizers) and a number of other representatives of the galvanizing industry. At this meeting Mr Piatkiewicz indicated that his members would be willing to assist with the work by providing facilities for field trials.

This was eventually followed up a number of years later with the organisation of visits to a number of UK galvanizers during 2003 and 2004. An overview of the work involved is given in section 9.

7 LABORATORY TESTS

7.1 FILTER BLANK LEVELS

For filter selection purposes, five membrane filters and two quartz filters were examined to determine their chloride blank levels. The filters concerned were:

Durapore	HVLP (hydrophilic)
Durapore	HVHP (hydrophobic)
Pall FP-450	PVDF
Pall GLA-5000	PVC
Pall DM-800	PVC-A
Pall Tissuquartz	Quartz
Whatman QMA	Quartz

Three filters of each type were leached with 10 ml water and the resulting solutions were analysed for chloride by IC on two occasions using separate calibrations. This produced a total of six replicate results for each filter type, as shown in Table 1.

Table 1 – Filter blanks levels for chloride

Filter	Chloride / μg						Mean	SD
	Replicate 1	Replicate 2	Replicate 3	Replicate 4	Replicate 5	Replicate 6		
HVLP	0.58	0.69	0.55	0.58	0.68	0.56	0.61	0.06
HVHP	0.15	0.25	0.22	0.15	0.23	0.21	0.20	0.04
FP-450	1.73	0.50	1.62	1.73	1.74	1.65	1.50	0.49
GLA-5000	0.11	0.15	0.09	0.10	0.13	0.06	0.11	0.03
DM-800	0.10	0.19	0.02	0.02	n.a.	0.09	0.08	0.07
Tissuquartz	0.10	0.01	n.a.	0.11	0.01	n.a.	0.06	0.05
QMA	0.01	0.01	0.01	0.01	0.01	n.a.	0.01	<0.01

n.a. = not analysed

The Pall GLA-5000 PVC filter was found to have a low chloride blank and, more importantly from the point of view of detection and quantification limits, it had the lowest blank variability of the membrane filters tested. Similarly, the Whatman QMA filter had the lowest blank and blank variability of the quartz fibre filters tested. It was therefore decided to use of GLA-5000 and QMA filters for the proposed HCl sampling exercises. The quantification limits for these filters, calculated as ten times the measured blank standard deviation, is approximately 0.3 μg and 0.02 μg respectively.

7.2 HCL COLLECTION EFFICIENCY

The collection efficiency of sodium carbonate-impregnated QMA filters was determined by exposing three-stage filter cassettes loaded with a GLA-5000 prefilter and two sodium carbonate-impregnated QMA filters to HCl vapour.

Sodium carbonate-impregnated QMA filters were prepared by pipetting 200 μl of a solution containing 5 g of sodium carbonate (Na_2CO_3) in 100 ml of water onto 25 mm diameter QMA filters and allowing them to dry for two hours.

Six three-stage Nucleopore filter cassettes were then constructed, each loaded with a GLA-5000 prefilter and two sodium carbonate-impregnated QMA filters. The loaded cassettes were then inserted into the centre orifices of one of HSL's multiport samplers and the unused orifices were blocked off.

A few ml of concentrated hydrochloric acid were dispensed onto a watch glass placed immediately below the inlet of the multiport sampler and the vacuum pump was switched on to draw air containing HCl vapour through the critical orifices, and hence the filter cassettes, at a rate of approximately 2 l/min. After two hours, the pump was switched off to discontinue sampling and the filter cassettes were removed from the multiport sampler.

The GLA-5000 filters and QMA filters were desorbed with 2 ml and 10 ml of deionised water, respectively, and the resulting sample solutions were analysed for chloride by IC. The results are given in Table 2.

Table 2 – HCl collection efficiency of sodium carbonate-impregnated QMA filters

Replicate no.	Chloride / μg			HCl collected on GLA-5000 pre-filter / %
	GLA-5000	QMA-1	QMA-2	
1	0.1	58.9	n.d.	0.2
2	0.2	48.8	n.d.	0.3
3	0.1	50.4	n.d.	0.3
4	0.2	60.5	n.d.	0.3
5	0.2	47.4	n.d.	0.4
6	0.2	62.5	n.d.	0.4
Mean	0.2	54.8	n.d.	0.3

n.d. = not detected

It is apparent that there is no significant retention of HCl on GLA-5000 pre-filters and that sodium hydroxide-impregnated QMA filters are 100 % effective at collecting HCl vapour.

Ideally, this work should be repeated with the filter cassettes exposed to HCl mist as well as vapour. However, such an experiment would be much more difficult to perform and it was decided not to attempt to do so.

7.3 INFLUENCE OF CO-SAMPLED PARTICULATE MATTER

Potential reduction in HCl collection efficiency by reaction with co-sampled particulate matter was assessed by exposing two-stage Nucleopore filter cassettes, each loaded with a spiked GLA-5000 pre-filter and a sodium carbonate-impregnated QMA filter, to HCl vapour.

Three GLA-5000 filters spiked with ferric oxide (Fe_2O_3) were prepared by pipetting a suspension of pure Fe_2O_3 in water onto the filters using a micropipette and allowing them to dry. Three GLA-5000 filters spiked with iron (Fe) and three GLA-5000 filters spiked with zinc oxide (ZnO) were prepared in a similar manner using suspensions of pure Fe powder and pure ZnO.

Sodium carbonate-impregnated QMA filters were prepared as described in 7.2.

Nine two-stage Nucleopore filter cassettes were then constructed, each loaded with a spiked GLA-5000 pre-filter and a sodium carbonate-impregnated QMA filter. An additional three such filter cassettes were loaded with welding fume samples collected on GLA-5000 filters and three blanks were prepared by loading filter cassettes with GLA-5000 filters that had no deposit on them. The loaded cassettes were then inserted into the centre orifices of one of HSL's multiport samplers and unused orifices blocked off.

The cassettes were exposed to air containing HCl vapour and the filters were desorbed and analysed for chloride by IC as described in 7.2. The results are given in Table 3.

Table 3 – HCl collection efficiency in the presence of co-sampled particulate matter

Material deposited on GLA-5000 prefilter	Total HCl collected / µg	HCl collected on GLA-5000 prefilter / %			
		Replicate	Mean	SD	RSD
No deposit	77	0.4			
	56	0.3	0.4	0.1	36
	82	0.5			
Fe ₂ O ₃	60	0.4			
	74	0.7	0.5	0.1	23
	61	0.5			
Fe	61	16			
	56	23	16	7	45
	69	9			
ZnO	46	52			
	42	66	54	11	21
	58	44			
Welding fume	213	81			
	125	59	71	11	16
	127	72			

As in the previous tests (see 7.2), it is apparent from the results obtained for the filters without a deposit that there is no significant retention of HCl on GLA-5000 pre-filters. Furthermore, the presence of Fe₂O₃ on the prefilter did not result in a low recovery of HCl. However, deposits of Fe, ZnO and welding fume on prefilters resulted, on average, in 16 %, 54 % and 71 % of the HCl to which the samplers were exposed being trapped on the prefilter. This suggests that exposures to HCl are likely to be underestimated if these substances are also present in the sampled air.

The above experiments were fairly rough and ready, having been carried out with limited control over the masses of potential interferents deposited on the prefilters, the concentration of HCl to which the samplers were exposed or the humidity of the air sampled. However, now that it is known that the potential for underestimation of HCl exposures is real, it is clear that further work is required to determine the extent of the potential interferences in a more controlled manner. Due to resource constraints it was decided not to carry out such work under JS2002837, but to organise a collaborative 'Volatile acids' sampling exercise with BGIA and INRS for the purpose. This exercise, which is scheduled to take place from 14-17 February 2006 at the BGIA test gas facility in Sankt Augustin, will be carried out under support job JS2003532, the 'Inorganic substances-in-air work programme'. It will not only further investigate the extent of potential interferences in HCl exposure measurement caused by possible reaction of HCl with co-sampled particulate matter, but also determine the performance characteristics of sorbent tube, filter and Radiello diffusive sampler methods for measurement of HCl (see 9.6.2).

Once again, as with the test carried out in 7.2, ideally this work should be repeated with the filter cassettes exposed to HCl mist as well as vapour. However, such an experiment would be much more difficult to perform and it was decided not to attempt to do so.

7.4 AMMONIUM CHLORIDE COLLECTION EFFICIENCY

Although the primary objective of this job was to develop a method for measurement of HCl in workplace air and use it to generate HCl exposure data for NEDB, it was decided that the planned field trials in galvanizing works should provide comprehensive information on all hazardous substances to which worker exposure could be significant. Hence, it was important that the sampling method used was suitable for collection of ammonium chloride as well as HCl.

The INRS method published in Métropol Fiche 013 [17] describes a sampling method for ammonia and ammonium salts that uses a PVC, PTFE or quartz fibre pre-filter to collect particulate ammonium salts and a back-up sulphuric acid-impregnated quartz fibre filter to trap ammonia. The back-up filter used in the INRS method is intended to collect ammonia present in the test atmosphere and/or ammonia from decomposition of ammonium salts. Decomposition of ammonium nitrate can occur to a certain extent during sampling, but there should not be a problem for ammonium chloride. Nevertheless, it was decided to carry out a quick test to verify that use of a back-up sulphuric acid-impregnated quartz fibre filter is unnecessary when sampling in galvanizing works. Potential loss of ammonium chloride by decomposition was determined by exposing GLA-5000 pre-filters with back-up sulphuric acid-impregnated QMA filters to sublimed ammonium chloride.

Similarly, ammonium chloride sublimates at 340 °C and has a significant vapour pressure at elevated temperatures, so theoretically some ammonium chloride could pass through a pre-filter during sampling. This is not expected to be a problem, but once again it was decided to carry out a quick test to check this out. The collection efficiency of GLA-5000 filters for ammonium chloride was determined by exposing GLA-5000 pre-filters with back-up water-containing impingers to sublimed ammonium chloride.

Sodium carbonate-impregnated quartz fibre filters were prepared by pipetting 200 µl of a solution containing 1.5 M sulphuric acid and 40 ml/l glycerol onto 25 mm diameter QMA filters and allowing them to dry for two hours.

A pair of two-stage Nucleopore filter cassettes was then constructed, each loaded with a GLA-5000 pre-filter and a sulphuric acid-impregnated QMA filter. In addition, two additional sampling trains were prepared, each comprising a single-stage Nucleopore filter cassette loaded with a GLA-5000 pre-filter and a back-up impinger containing 10 ml of deionised water. The two-stage filter cassettes and the filter cassette and impinger sampling trains were attached to Gilian pumps and air samples were collected at a flow rate of 1 l/min over a heated watch glass containing ammonium chloride for a period of approximately 20 minutes.

The GLA-5000 filters and QMA filters were desorbed with 10 ml of deionised water and the resulting sample solutions and the impinger solutions were analysed by IC for ammonium and chloride (for confirmation). The results are given in Table 4.

Table 4 – Ammonium chloride collection characteristics of GLA-5000 pre-filters

Sampling	Replicate no.	Chloride (μg)		
		GLA-5000	QMA	Water
Two-stage filter cassette	1	26.9	n.d.	---
	2	43.0	n.d.	---
Filter cassette and impinger	1	59.3	---	12.4*
	2	14.9	---	3.9*

Sampling	Replicate no.	Ammonium (μg)		
		GLA-5000	QMA	Water
Two-stage filter cassette	1	15.7	n.d.	---
	2	17.8	n.d.	---
Filter cassette and impinger	1	26.3	---	n.d.
	2	6.3	---	n.d.

n.d. = not detected

* attributed to chloride contamination

The results for the two-stage filter cassette show that, as expected, there is no decomposition of ammonium chloride on GLA-5000 pre-filters, as no ammonium was found on the sulphuric acid-impregnated QMA filter.

Likewise, the results for the filter cassette and impinger sampling trains indicate that there is no breakthrough of ammonium chloride from the GLA-5000 pre-filters, the chloride found in the impingers probably being due to contaminated glassware

8 METHOD SELECTION

It was decided that the primary method used for collection of personal exposure data would be based on the two-stage filter method described by the INRS in Métropol Fiche 009 *Anions Minéraux* [3]. Sampling would be carried out using GLA-5000 pre-filters mounted in IOM samplers, backed up with in-line sodium carbonate-treated QMA filters. This method was considered to exhibit no obvious shortcomings in relation to the silica gel tube method, which has a significant drawback in that the particle size collection characteristics of a sorbent tube have been shown [9] not match the inhalable convention.

However, the extent to which HCl is present in the form of a mist in galvanizing works is unknown, so it was decided to take some samples with sorbent tubes for comparative purposes. If HCl is present mostly in the gaseous form, results obtained using the two-stage filter method and the sorbent method should be quite similar. It was also decided to investigate the performance of diffusive samplers for HCl manufactured by Radiello, which might be expected to perform well if HCl is present in the gaseous phase. Nearly all of these parallel measurements were carried out at fixed points, so as not to overburden workers with pumps and other sampling equipment.

9 FIELD SAMPLING VISITS TO UK GALVANIZERS

9.1 PURPOSE

The purpose of the field sampling visits was to carry out workplace air measurements for the range of chemical agents to which workers in the galvanizing industry are exposed in order to (i) provide exposure data for NEDB and (ii) compare the performance of different methods for sampling hydrogen chloride and hydrochloric acid mist.

9.2 HOT DIP GALVANIZING

9.2.1 Overview

Hot dip galvanizing is a process that is used to coat iron or steel with a protective layer of zinc, giving it a long corrosion-free life. It typically involves putting the work pieces through a number of processes, including jiggging, degreasing in alkali, pickling in acid, fluxing, dipping in hot molten zinc and de-jiggging. The range of plants visited covered work of all sizes, ranging from small items such as nuts and bolts, through medium size work pieces such as decorative fencing, to large structural supports and beams.

9.2.2 'Jiggging' or 'black end prep'

Prior to processing, larger items to be galvanized are usually bundled together, whereas medium-sized items are attached to metal frames, or 'jigs', using wire hooks and chains, an operation referred to as 'jiggging'. Smaller items are usually placed in steel mesh crates. The work pieces are normally then moved through the production line using overhead cranes. The area in which work pieces are prepared for galvanizing is often referred to as the 'black end' of the site and the process of preparing work pieces for treatment is sometimes called 'black end prep'.

9.2.3 Degreasing

Work pieces to be galvanized have to be free from contamination. The first stage in the chemical cleaning process used at many, but not all, galvanizing plants is degreasing. This involves removing any oil or grease by immersion in a tank containing alkaline solution. These tanks were not fitted with local exhaust ventilation (LEV) at any of the sites visited.

9.2.4 Pickling

The next stage in the cleaning process involves immersion of the work pieces in dilute hydrochloric acid to remove rust and scale, a process known as 'pickling'. This process releases bubbles of gas that, as they break the surface of the liquid, cause hydrochloric acid mist to be formed above the pickling tanks. These tanks were not fitted with LEV at any of the sites visited, so the resulting hydrochloric acid mist, except for large droplets that fall back into the tank through sedimentation, in all cases entered the general atmosphere of the workplace. HCl is a gas at room temperature and it is therefore vaporised from the hydrochloric acid mist to an unknown, but probably fairly large, extent. Employees working at pickling tanks, commonly referred to as 'picklers', are therefore exposed to a mixture of hydrogen chloride gas and hydrochloric acid mist

9.2.5 Prefluxing

After pickling the work pieces are coated with flux to improve the efficiency of the galvanizing process and thus improve the quality of the finished product. The work pieces are first rinsed by dipping in water and then immersed in a flux solution containing ammonium, zinc and sometimes potassium chlorides. The temperature of preflux tanks is usually in the region of 60-70 °C, so the work pieces dry fairly quickly on removal from the tanks. However, the work pieces are sometimes placed in a drying pit after removal from the preflux tank in order to enhance the effectiveness of drying process. This reduces the amount of water on the work pieces when they are dipped in the molten zinc, thus helping to minimise spatter. The preflux tanks were not fitted with LEV, except at site 5.

9.2.6 Galvanizing

Cleaned and prefluxed work pieces are galvanized by dipping in baths containing molten zinc, which is maintained at temperature of approximately 450 °C, and this leads to the release of ZnO, ZnCl₂ and NH₄Cl fumes. At all but one of the sites visited, the baths were fully enclosed and LEV was effective when the work pieces were lowered into the molten zinc, the stage at which by far the greatest evolution of fume occurs. Sometimes the enclosures were moved from over the baths when the galvanising process was complete, so that workers could skim 'ash' from the surface of the molten zinc; whilst other enclosures had side screens or doors that could be raised or opened to allow this operation to be carried out. Clearing of ash from around the work pieces as they are removed from the galvanizing bath ensures that the finished product has a smooth attractive surface finish.

At site 3, smaller items that had gone through the cleaning process in wire baskets were transferred to perforated metal drums before dipping and excess zinc was removed by centrifugation immediately after removal from the galvanizing bath.

9.2.7 Quenching

After removal from the galvanizing bath the work pieces have a smooth, shiny attractive surface finish that very quickly becomes dull and grey as the zinc surface coating oxidises in the air. In order to preserve the shiny finish, the work pieces can be 'quenched' in a chromate bath immediately after galvanising. This process is, however, somewhat specialised and was in use at only one or two of the sites visited.

9.2.8 White end 'de-jigging'

Finally, after the galvanizing process is complete, any wires and chains securing work pieces to 'jigs' are removed in the 'white end' of the galvanizing plant, an operation often referred to as 'de-jigging'.

9.3 SUBSTANCES TO WHICH GALVANIZING WORKERS ARE POTENTIALLY EXPOSED

9.3.1 Hydrogen chloride

WEL: 1 ppm, 8-hour TWA; 5 ppm, 15-min STEL

The pickling process is a potential source of hydrogen chloride gas and/or hydrochloric acid mist, for which there is a workplace exposure limit (WEL) of 1 ppm, 8-hour time weighted average (TWA) and a short-term exposure limit (STEL) of 5 ppm. According to EH 40, 1 ppm is equivalent to 2 mg m^{-3} for HCl, but in fact 1 ppm of HCl is almost exactly equal to 1.5 mg m^{-3} of HCl at ambient temperature and pressure, so this is the limit value with which the results of personal exposure measurements have been compared.

9.3.2 Zinc chloride

WEL: 1 mg m^{-3} , 8-hour TWA; 2 mg m^{-3} , 15-min STEL

ZnCl_2 is a component of the flux applied to work pieces to improve the efficiency of the galvanizing process and promote the quality of the finished product. It may be released into the air during the galvanizing process and it could also be formed by reaction of ZnO with HCl, either in the air or on the filter used for sample collection. Results of personal exposure measurements for ZnCl_2 have been compared with the WEL of 1 mg m^{-3} , 8-hour TWA.

9.3.3 Zinc oxide fume

No WEL. Former OES: 5 mg m^{-3} , 8-hour TWA; 10 mg m^{-3} , 15-min STEL

ZnO is formed during the galvanizing process. There is no WEL for this substance, so results of personal exposure measurements for ZnO have been compared with the former occupational exposure standard (OES) for ZnO fume, which was 5 mg m^{-3} , 8-hour TWA. However, it should be noted that in fact, ZnO it is unlikely to be released as fume, since the temperature of the molten zinc in galvanizing baths is approximately $450 \text{ }^\circ\text{C}$ and the boiling point of zinc is significantly higher than this at $907 \text{ }^\circ\text{C}$.

9.3.4 Ammonium chloride

WEL: 10 mg m^{-3} , 8-hour TWA; 20 mg m^{-3} , 15-min STEL

NH_4Cl , like ZnCl_2 , is a component of the flux applied to work pieces, and it may also be released into the air during the galvanizing process. Results of personal exposure measurements for NH_4Cl , have been compared with the WEL of 10 mg m^{-3} , 8-hour TWA.

9.4 WORK PATTERNS

At all the sites visited, employees worked either a two-shift pattern or a three-shift pattern. Perhaps more significantly, at most sites workers had a specific job function, i.e. jigger, pickler, galvanizer, forklift truck driver etc. Only at site 6 was this not the case. At this site, job rotation was applied, so that workers spent about one quarter of each shift as picklers, one quarter as galvanizers and the rest of the shift on other duties. This will have the effective of reducing their TWA exposure. However, for reasons of comparability, the results given in the table in Appendix A are not time-weighted.

9.5 SAMPLING AND ANALYSIS

9.5.1 Personal exposure measurements

Personal exposure measurements of HCl, ZnCl₂, NH₄Cl and ZnO were carried out using a sampling train consisting of a GLA-5000 pre-filter mounted in an IOM head, backed up with a sodium carbonate-treated QMA filter mounted in a Gelman in-line filter holder. This is more or less identical to the two-stage filter method described by the INRS in Métropol Fiche 009 *Anions Minéraux* [3]. Personal sampling was carried out in the workers' breathing zone at a flow rate of 2 l min⁻¹ and fixed-point samples were collected in the pickling areas

The PVC filters were leached with water and the resulting solutions analysed for ammonium and chloride by IC and for water-soluble zinc by inductively coupled plasma – atomic emission spectrometry (ICP-AES). The ammonium results were used to calculate personal exposure to NH₄Cl and the water-soluble zinc results were used to calculate personal exposure to ZnCl₂. The chloride results were also used to estimate personal exposure to NH₄Cl as a crosscheck, making the assumption that all chloride except that associated with zinc was present in this form. The PVC filters were then leached with hydrochloric acid and the resulting sample solutions analysed for acid-soluble zinc by ICP-AES. The acid-soluble zinc results were used to calculate personal exposure to ZnO.

The treated QMA filters were leached with water, the resulting sample solutions analysed for chloride by IC and the results used to calculate personal exposure to HCl.

9.5.2 Fixed-point (static) measurements

In addition to personal sampling, fixed-point (static) sampling was carried out at a number of positions within the workplace, both to determine the concentration of hazardous substances in the air at these positions and to compare the performance of different methods for sampling HCl.

Static samples were collected in the same way as personal samples, but additional samples were collected at the same positions using washed silica gel sorbent tubes, as described by the NIOSH in Method 7903 *Acids, Inorganic* [1]. Radiello diffusive samplers, consisting of a silica gel collection cartridge contained within an outer diffusive body, were also deployed.

The silica gel sorbent tubes and the silica gel collection cartridges used in the Radiello samplers were desorbed with water and analysed for chloride by IC. The front and back-up sections of silica gel in the each sorbent tube and the glass fibre plug that precedes the front section of silica gel were analysed separately.

9.6 RESULTS AND DISCUSSION

9.6.1 Personal exposure measurements

The results of the personal exposure measurements made in the nine sampling exercises are summarised, site by site, in Appendix A; and an overall summary of personal exposure measurements is given in Appendix B. The tables in both of these appendices give separate minimum and maximum TWA exposures for jiggers, pickers and galvanizers, together with mean and median exposures for each group of workers. The median values probably give a better indication of typical exposure than the means.

From Appendix B it can be seen that, as expected, picklers had the highest exposure to HCl. Results of long-term HCl exposure measurements for picklers ranged from 0.02 mg m⁻³ to 2.22 mg m⁻³, with a median value of 0.55 mg m⁻³, which is approximately one third of the WEL of 1.5 mg m⁻³ (see 9.3.1). Personal exposure measurement results for other groups of workers were much lower, with median exposures for jiggers and galvanizers being 0.04 mg m⁻³ and 0.08 mg m⁻³, respectively.

As expected, galvanizers had the highest exposure to ZnCl₂. Results of long-term ZnCl₂ exposure measurements for galvanizers ranged from 0.15 mg m⁻³ to 1.84 mg m⁻³, with a median value of 0.44 mg m⁻³, which is approximately one half of the WEL of 1 mg m⁻³ (see 9.3.2). Personal exposure measurement results for other groups of workers were much lower, with median exposures for jiggers and galvanizers being 0.17 mg m⁻³ and 0.19 mg m⁻³, respectively.

Similarly, galvanizers had the highest exposure to ZnO. Results of long-term ZnO exposure measurements for galvanizers ranged from 0.03 mg m⁻³ to 1.22 mg m⁻³, with a median value of 0.17 mg m⁻³, which is less than one tenth of the former OES of 5 mg m⁻³ (see 9.3.3). Personal exposure measurement results for other groups of workers were again lower, with median exposures for both jiggers and picklers being 0.02 mg m⁻³.

Finally, galvanizers also had the highest exposure to NH₄Cl. Results of long-term NH₄Cl exposure measurements for galvanizers ranged from 0.03 mg m⁻³ to 2.14 mg m⁻³, with a median value of 0.36 mg m⁻³, which is very low in comparison with the WEL of 10 mg m⁻³ (see 9.3.3). Personal exposure measurement results for other groups of workers were lower still, with median exposures for jiggers and picklers being 0.10 mg m⁻³ and 0.17 mg m⁻³, respectively.

9.6.2 Fixed-point (static) measurements

Appendix C gives a summary of the results of fixed-point (static) measurements made in the vicinity of pickling baths. Of primary interest in this case are HCl results, others being provided essentially for completeness. The median of HCl measurements made near pickling baths (0.85 mg m⁻³) was not dissimilar to the median HCl exposure for picklers (0.55 mg m⁻³), but some of the higher HCl concentrations found near pickling baths were significantly higher than the highest HCl exposure measurement, by a factor of up to about four. Consequently, consideration was given to whether there could be a short-term exposure problem with HCl. However, only one fixed-point measurement result exceeded the STEL of 7.5 mg m⁻³ (see 9.3.1), and none if results are compared with the figure of 10 mg m⁻³ actually listed in EH 40, which is incorrectly converted from the 15-min WEL of 5 ppm. Hence, there is little risk that the exposure of picklers will exceed the STEL.

Interpretation of the results of the parallel sampling carried out with silica gel tubes and Radiello diffusive samplers was difficult. It is well known that it is difficult to assess the relative performance of samplers in the field because there can be large spatial variation in the concentration of workplace air pollutants. Nevertheless, it was hoped that the results would give an indication of the likely intercomparability of results obtained by the different methods tested. However, a further, unexpected, problem was encountered with the silica gel tubes, in that it was found that a substantial proportion of HCl was collected on the glass wool plugs that retain the sorbent in place. This became evident when results obtained using the two-stage filter method, which showed that the majority of the chloride was present in the sampled air as HCl, were compared with results obtained using silica gel tubes, for which nearly all the chloride was found to be on the glass wool plug that should have collected only particulate chloride. It was concluded that the only comparison that could usefully be made was to calculate the total chloride collected on the GLA-5000 prefilters and back-up sodium carbonate-treated QMA filters and compare this with the total chloride collected on the silica gel tubes.

There was a very wide scatter of paired results (see Appendix D), as might be anticipated for a field comparison of measurement methods, but it was found that on average the silica gel tubes collected around 85 % of the chloride collected on the GLA-5000 prefilter and back-up sodium carbonate-treated QMA filters. This was as expected, since the particle size collection characteristics of silica gel tubes do not match the inhalable convention (see 4.2) and they will therefore tend to under sample HCl mist and particulate chlorides.

There was also a very wide scatter of paired results for the Radiello diffusive samplers (see Appendix D). On average, it was found that the Radiello samplers, which were used in only the first three sampling visits, collected around 155 % of the HCl collected on the back-up impregnated QMA filters. This high figure could be due to contamination of the external diffusive body of the samplers, which were found to be prone to such a problem when positioned in the vicinity of pickling tanks. If hydrochloric acid droplets deposit on the outside of the samplers, results will be compromised. Hence, they are probably not best suited to use in the determination of HCl in galvanizing plants.

Field exercises are not ideal for comparing measurement methods. Therefore, a collaborative 'Volatile acids' sampling exercise has been organised with BGIA and INRS to determine the performance characteristics of sorbent tube, filter and Radiello diffusive sampler methods for measurement of HCl. This will include testing the methods with and without prefilters over a range of HCl concentrations and at different humidity conditions. However, it

9.6.3 Comparison with other published data

A review of the literature revealed a dearth of published data on worker exposure in the galvanizing industry. Data found were in an occupational hygiene section report by Ramsey [18], dating from 1980, and there were other data published in papers by Jackson *et al* [12], Remijn *et al* [13] and Lamont *et al* [14]. Appendix E contains a summary of the results obtained in this work and those obtained by Ramsey, Jackson and Remijn. Lamont's data are entirely fixed-point measurement results carried out for method evaluation purposes and have not been included in the tabulation. It can be seen from Appendix E that exposure data reported by the various workers is remarkably similar for HCl, ZnCl₂ and ZnO, especially taking into consideration the time span (1980–2004) and the sampling difficulties. There is, however, some indication that NH₄Cl exposures are now rather lower than they have been in the past.

10 CONCLUSIONS

A review of available methods for measurement of HCl and other chemical agents to which workers in the galvanizing industry are exposed revealed a number of areas of potential concern with existing published methods. These included issues with particle size-collection characteristics of sorbent tubes for hydrochloric acid mist, HCl collection efficiency, possible reaction of HCl with co-sampled particulate matter, possible reaction of sulphuric acid mist with co-sampled chloride-containing particulate matter, NH_4Cl collection efficiency and the effectiveness with which ZnCl_2 and ZnO are separated on the basis of their widely different solubilities. The most important of these issues were investigated and it was concluded that the best method for sampling HCl and other chemical agents to which workers in the galvanizing industry are exposed is a two-stage filter method, using a GLA-5000 PVC prefilter to collect ZnCl_2 , ZnO and NH_4Cl and a sodium carbonate-impregnated QMA quartz fibre filter to trap HCl.

Field sampling visits were carried out at nine galvanizing plants and these generated a considerable volume of exposure data for NEDB. Picklers were found to experience the highest exposure to HCl, whilst galvanizers had the highest exposures to ZnCl_2 , ZnO and NH_4Cl . The median values of the exposures concerned were 0.55 mg m^{-3} , 0.44 mg m^{-3} , 0.17 mg m^{-3} and 0.36 mg m^{-3} , respectively, all of which are well below the relevant exposure limits of 1.5 mg m^{-3} for HCl (WEL), 1 mg m^{-3} for ZnCl_2 (WEL), 5 mg m^{-3} for ZnO (former OES) and 10 mg m^{-3} for NH_4Cl (WEL). However, maximum exposures measured for HCl (2.22 mg m^{-3}) and ZnCl_2 (1.84 mg m^{-3}) were above the WELs and there is therefore scope for improvement in control measures. The exposure data arising from the field visits (nearly 400 results) have been added to NEDB, along with summary reports for each of the galvanizing plants visited.

The field sampling visits also provided an indication of how the performance of the sorbent tube and two-stage filter methods for HCl compare. The scatter of paired results was very wide, as might be anticipated for a field comparison of measurement methods, but on average silica gel tubes were found to collect around 85% of the HCl sampled using the two-stage filter method. This was as expected, since the particle size collection characteristics of silica gel tubes do not match the inhalable convention and they will therefore tend to under sample HCl mist and particulate chlorides. Radiello diffusive samplers were found to over sample in comparison to the two-stage filter method, but it seems likely that this was due to contamination of the external diffusive body of the samplers, which appears to be drawback of this type of device.

Further work is required to determine the performance characteristics of available methods before a definitive recommendation for a method for HCl measurement can be made. A collaborative 'Volatile acids' sampling exercise has therefore been organised with BGIA and INRS to determine the performance characteristics of filter, sorbent tube and Radiello diffusive sampler methods for measurement of HCl. This exercise, which is scheduled to take place from 14-17 February 2006 at the BGIA test gas facility in Sankt Augustin, will be carried out under support job JS2003532, the 'Inorganic substances-in-air work programme'. It will also investigate further the extent of potential interferences in HCl exposure measurement caused by reaction of HCl with co-sampled particulate matter (see 7.3).

11 APPENDICES

APPENDIX A — PERSONAL EXPOSURE MEASUREMENTS: RESULTS SUMMARIES, SITE BY SITE

Site	Employees exposed	Type of work pieces	Exposure measurements	Ventilation	TWA exposure *	HCl / mg/m ³	ZnCl ₂ / mg/m ³	ZnO / mg/m ³	NH ₄ Cl / mg/m ³
1	Large site, 55 shop floor workers, 40 potentially exposed.	Very large items such as lamp posts, mobile phone masts, etc.	Jiggers (4)	Good natural ventilation (open-ended building)	Minimum	0.02	0.17	0.13	0.36
					Maximum	0.06	0.34	0.27	0.41
					Mean	0.04	0.25	0.18	0.39
					Median	0.03	0.24	0.17	0.39
			Picklers (4)	No LEV fitted to picking or preflux tanks	Minimum	0.27	0.02	< 0.01	0.09
					Maximum	0.73	0.18	0.11	0.28
					Mean	0.50	0.09	0.05	0.16
					Median	0.50	0.07	0.05	0.14
			Galvanizers (4)	Single galvanizing bath, fully enclosed, equipped with LEV that was effective when doors closed for dipping	Minimum	0.01	0.17	0.15	0.14
					Maximum	0.04	0.38	0.33	0.19
					Mean	0.03	0.28	0.22	0.16
					Median	0.02	0.29	0.20	0.15
2	Large site, 72 shop floor workers, 54 potentially exposed	Medium to large items, varying from metal fabrications such as garden gates to smaller items weighing ~1-2 kg.	Jiggers (6)	Good natural ventilation (open-ended building)	Minimum	0.02	0.02	< 0.01	0.02
					Maximum	0.05	0.10	0.07	0.15
					Mean	0.03	0.06	0.03	0.08
					Median	0.03	0.05	0.02	0.05
			Picklers (3)	No LEV fitted to degreasing, picking or preflux tanks	Minimum	0.02	0.04	< 0.01	0.07
					Maximum	0.26	0.15	0.05	0.16
					Mean	0.12	0.09	0.02	0.11
					Median	0.06	0.08	0.02	0.11
			Galvanizers (5)	2 galvanizing baths, 1 fully enclosed, 1 with moveable enclosure, equipped with LEV that was effective when doors closed for dipping	Minimum	0.02	0.15	0.03	0.12
					Maximum	0.30	0.63	0.86	0.42
					Mean	0.10	0.35	0.34	0.25
					Median	0.08	0.33	0.23	0.19

Site	Employees exposed	Type of work pieces	Exposure measurements	Ventilation	TWA exposure *	HCl / mg/m ³	ZnCl ₂ / mg/m ³	ZnO / mg/m ³	NH ₄ Cl / mg/m ³
3	Medium sized site, 64 shop floor workers, 51 potentially exposed.	Small items such as nuts, washers, forgings, fabrications, presswork and chain.	Jiggers (5)	General ventilation was relatively poor and insufficient to prevent build-up of a significant visible haze	Minimum	0.03	0.23	0.02	0.53
					Maximum	0.10	1.69	0.13	2.53
					Mean	0.05	0.65	0.05	1.51
					Median	0.04	0.46	0.03	1.41
			Picklers (4)	No LEV fitted to degreasing, picking or preflux tanks	Minimum	0.04	0.18	< 0.01	1.05
					Maximum	2.22	0.55	0.02	2.89
					Mean	0.78	0.33	< 0.01	2.00
					Median	0.44	0.31	< 0.01	2.03
			Galvanizers (7)	3 galvanizing baths, 2 with surface extraction and 1 with partially-enclosed extracted booth	Minimum	0.03	0.55	0.03	1.08
					Maximum	0.11	1.64	0.33	2.14
					Mean	0.06	0.95	0.15	1.50
					Median	0.05	0.79	0.13	1.41
4	Large site, 40 workers on site, 20 potentially exposed	Wide range, from relatively small items to large items of structural steelwork	Jiggers (3)	Reasonable natural ventilation (large open doors at each end of building and roof vents))	Minimum	< 0.01	0.23	n.a.	0.01
					Maximum	< 0.01	0.34	n.a.	0.02
					Mean	< 0.01	0.29	n.a.	0.01
					Median	< 0.01	0.31	n.a.	0.01
			Picklers (2)	No LEV fitted to degreasing, picking or preflux tanks	Minimum	0.53	0.22	< 0.01	0.14
					Maximum	0.96	0.23	0.02	0.16
					Mean	0.74	0.22	0.01	0.15
					Median	0.74	0.22	0.01	0.15
			Galvanizers (3)	Single galvanizing bath, fully enclosed, but without LEV	Minimum	0.03	0.48	0.18	0.22
					Maximum	0.09	0.68	1.03	0.28
					Mean	0.06	0.56	0.50	0.24
					Median	0.07	0.51	0.29	0.23

Site	Employees exposed	Type of work pieces	Exposure measurements	Ventilation	TWA exposure *	HCl / mg/m ³	ZnCl ₂ / mg/m ³	ZnO / mg/m ³	NH ₄ Cl / mg/m ³
5	Medium sized site, approximately 20 shop floor workers	Medium sized items.	Jiggers (0)	Good natural ventilation (large open doors at each end of building and roof vents)	Minimum				
					Maximum				
					Mean				
					Median				
			Picklers (2)	No LEV fitted to degreasing or picking tanks. Preflux tank equipped with high-level, effective, LEV	Minimum	0.43	0.40	0.13	0.09
					Maximum	0.58	0.69	0.31	0.11
					Mean	0.51	0.54	0.22	0.10
					Median	0.51	0.54	0.22	0.10
			Galvanizers (2)	Single galvanizing bath, fully enclosed, equipped with LEV that was effective when doors closed for dipping	Minimum	< 0.01	0.30	0.34	0.03
					Maximum	< 0.01	0.30	1.22	0.05
					Mean	< 0.01	0.30	0.78	0.04
					Median	< 0.01	0.30	0.78	0.04
6	Very large site, 320 workers, 20 potentially exposed in the galvanizing plant	Medium to large items	Jiggers (0)	Natural ventilation (large open doors at each end of building and roof vents) was insufficient to prevent build-up of a visible haze	Minimum				
					Maximum				
					Mean				
					Median				
			Picklers (8)	No LEV fitted to picking or preflux tanks	Minimum	0.29	0.12	0.02	0.13
					Maximum	1.27	0.48	0.09	0.56
					Mean	0.62	0.26	0.04	0.36
					Median	0.56	0.26	0.02	0.37
			Galvanizers (5)	Single galvanizing bath, equipped with moveable LEV enclosure that was effective when doors closed for dipping	Minimum	0.15	0.44	0.06	0.47
					Maximum	0.15	1.84	0.29	1.60
					Mean	0.15	1.01	0.16	1.01
					Median	0.15	1.13	0.12	1.09

Site	Employees exposed	Type of work pieces	Exposure measurements	Ventilation	TWA exposure *	HCl / mg/m ³	ZnCl ₂ / mg/m ³	ZnO / mg/m ³	NH ₄ Cl / mg/m ³
7	Medium sized site, 55 shop floor workers, 40 potentially exposed.	Medium to large items such as lamp posts, general structural steel work, fencing, gates and guardrails	Jiggers (6)	Good natural general ventilation in jiggling and de-jogging areas (large open doors at each end of the L-shaped workshop)	Minimum	0.22	0.06	< 0.01	0.05
					Maximum	0.41	0.08	0.01	0.10
					Mean	0.30	0.07	< 0.01	0.08
					Median	0.29	0.07	< 0.01	0.08
			Picklers (2)	No LEV fitted to picking or preflux tanks. Natural ventilation in the vicinity of pre-flux tanks was not good due to L-shape of workshop	Minimum	0.80	0.05	< 0.01	0.07
					Maximum	1.53	0.06	< 0.01	0.08
					Mean	1.17	0.06	< 0.01	0.07
					Median	1.17	0.06	< 0.01	0.07
			Galvanizers (1 HCl; 2 ZnCl ₂ , ZnO and NH ₄ Cl)	Single galvanizing bath, fully enclosed, equipped with LEV that was effective when doors closed for dipping	Minimum	1.53	0.37	0.16	0.18
					Maximum	1.53	0.74	0.21	0.25
					Mean	1.53	0.55	0.19	0.22
					Median	1.53	0.55	0.19	0.22
8	Medium sized site, 30 workers on site, 24 potentially exposed	Medium sized items.	Jiggers (2)	Natural ventilation (large open doors at each end of building) was insufficient to prevent build-up of a visible haze	Minimum	0.11	0.19	< 0.01	0.23
					Maximum	0.40	0.23	0.20	0.39
					Mean	0.26	0.21	0.10	0.31
					Median	0.26	0.21	0.10	0.31
			Picklers (2)	No LEV fitted to picking or preflux tanks	Minimum	0.52	0.04	0.01	0.06
					Maximum	0.74	0.28	0.02	0.60
					Mean	0.63	0.16	0.01	0.33
					Median	0.63	0.16	0.01	0.33
			Galvanizers (4)	Single galvanizing bath, fully enclosed, equipped with LEV that was effective when doors closed for dipping	Minimum	0.10	0.28	0.09	0.39
					Maximum	0.40	0.37	0.28	0.54
					Mean	0.22	0.33	0.14	0.45
					Median	0.19	0.34	0.10	0.44

Site	Employees exposed	Type of work pieces	Exposure measurements	Ventilation	TWA exposure *	HCl / mg/m ³	ZnCl ₂ / mg/m ³	ZnO / mg/m ³	NH ₄ Cl / mg/m ³
9	Large site, 55 workers, 27 potentially exposed	Medium to large items	Jiggers (3)	Good natural ventilation (large open doors at each end of building)	Minimum	0.01	0.08	0.02	0.06
					Maximum	0.12	0.18	0.07	0.10
					Mean	0.05	0.13	0.04	0.08
					Median	0.01	0.11	0.02	0.09
			Picklers (3)	No LEV fitted to picking or preflux tanks	Minimum	0.49	0.09	< 0.01	0.06
					Maximum	1.70	0.28	0.06	0.21
					Mean	1.27	0.17	0.03	0.12
					Median	1.62	0.14	0.01	0.09
			Galvanizers (2)	Single galvanizing bath, fully enclosed, equipped with LEV that was effective when doors closed for dipping	Minimum	0.34	0.28	0.04	0.27
					Maximum	0.62	0.31	0.07	0.34
					Mean	0.48	0.29	0.06	0.30
					Median	0.48	0.29	0.06	0.30

* For comparability, results reported for Site 6 are not TWAs, as the working pattern was significantly different to other sites, with frequent worker rotation
n.a. ZnO results not available for Site 4 jiggers because exposure was masked by metallic zinc from fettling of the finished items using hand held grinders

APPENDIX B — PERSONAL EXPOSURE MEASUREMENTS: OVERALL RESULTS SUMMARY

Employees exposed	Type of work pieces	Exposure measurements	Ventilation	WEL (8h TWA)				
				HCl / mg/m ³	ZnCl ₂ / mg/m ³	ZnO / mg/m ³	NH ₄ Cl / mg/m ³	
				1.5*	1	(5)**	10	
Approximately 300 potentially exposed workers in 9 galvanizing plants, averaging around 30 potentially exposed worker per site	From small items such as nuts and bolts to large items such as lamp posts	Jiggers (29)	Most galvanizing baths had good natural ventilation (open-ended buildings or buildings with large open doors)	Minimum TWA exposure	< 0.01	0.02	< 0.01	0.01
				Maximum TWA exposure	0.41	1.69	0.27	2.53
				Mean TWA exposure	0.11	0.23	0.06	0.38
				Median TWA exposure	0.04	0.17	0.02	0.10
		Picklers (30)	No LEV fitted to picking or preflux tanks in all but one plants	Minimum TWA exposure	0.02	0.02	< 0.01	0.06
				Maximum TWA exposure	2.22	0.69	0.31	2.89
				Mean TWA exposure	0.68	0.22	0.04	0.45
				Median TWA exposure	0.55	0.19	0.02	0.17
		Galvanizers (34)	Most galvanizing baths fully enclosed, equipped with LEV that was effective when doors closed for dipping	Minimum TWA exposure	< 0.01	0.15	0.03	0.03
				Maximum TWA exposure	1.53	1.84	1.22	2.14
				Mean TWA exposure	0.17	0.58	0.25	0.62
				Median TWA exposure	0.08	0.44	0.17	0.36

* According to EH 40, 1 ppm is equivalent to 2 mg m⁻³ for HCl, but in fact 1 ppm HCl is almost exactly equal to 1.5 mg m⁻³ HCl at ambient temperature and pressure, so this is the limit value with which results of personal exposure measurements have been compared.

** There is no WEL for ZnO. Results of personal exposure measurements compared with the former OES for ZnO fume.

APPENDIX C — SUMMARY OF FIXED-POINT (STATIC) MEASUREMENTS NEAR PICKLING BATHS

	HCl / mg/m ³	ZnCl ₂ / mg/m ³	ZnO / mg/m ³	NH ₄ Cl / mg/m ³
STEL	7.5*	2	(10)**	20
Minimum TWA exposure	0.12	<0.01	<0.01	<0.01
Maximum TWA exposure	8.75	0.61	0.06	2.21
Mean TWA exposure	1.84	0.14	0.01	0.30
Median TWA exposure	0.85	0.11	0.01	0.12

* According to EH 40, 1 ppm is equivalent to 2 mg m⁻³ for HCl, but in fact 1 ppm HCl is almost exactly equal to 1.5 mg m⁻³ HCl at ambient temperature and pressure, so this is the limit value with which results of personal exposure measurements have been compared.

** There is no WEL for ZnO. Results of personal exposure measurements compared with the former OES for ZnO fume.

APPENDIX D — COMPARISON OF SILICA GEL TUBES AND RADIELLO DIFFUSIVE SAMPLERS WITH THE PERFORMANCE OF THE TWO-STAGE FILTER SAMPLING METHOD

	Ratio of silica gel tube results to GLA-5000 prefilter and Na ₂ CO ₃ -treated QMA filter results / % (as total chloride)	Ratio of Radiello results to Na ₂ CO ₃ -treated QMA filter results / % (as total chloride)
Minimum	28%	92%
Maximum	196%	228%
Mean	84%	156%
Standard deviation	35%	41%

APPENDIX E — COMPARISON WITH PREVIOUSLY PUBLISHED DATA

Source of data		HCl	ZnCl ₂	ZnO	NH ₄ Cl
This work	Minimum concentration / mg/m ³	<0.1	<0.1	<0.1	<0.1
	Maximum concentration / mg/m ³	2.2	1.8	1.2	2.9
	Mean concentration / mg/m ³	0.3	0.4	0.1	0.5
Ramsey [18]	Minimum concentration / mg/m ³	-	-	-	-
	Maximum concentration / mg/m ³	1.5	1.4	1.0	-
	Mean concentration / mg/m ³	0.4	0.3	0.2	2.8
Jackson <i>et al</i> [12]	Minimum concentration / mg/m ³	0.2	<0.1	<0.1	0.2
	Maximum concentration / mg/m ³	2.7	0.8	0.7	6.5
	Mean concentration / mg/m ³	0.5	0.2	0.1	0.9
Remijn <i>et al</i> [13]	Minimum concentration / mg/m ³	1.8*	0.2	-	-
	Maximum concentration / mg/m ³	5.3*	0.9	-	-
	Mean concentration / mg/m ³	3.4*	0.5	-	-

* Results are from fixed-point measurements

12 REFERENCES

- [1] US National Institute of Occupational Safety and Health (1994) *NIOSH Manual of Analytical Methods, 4th Edition Method 7903 Acids, Inorganic* DHHS (NIOSH) Publication 94-113 <http://www.cdc.gov/niosh/nmam/>
- [2] Deutsche Forschungsgemeinschaft (2002) *Volatile inorganic acids (HCL, HBr, HNO₃) in Analyses of hazardous substances in air* Volume 6 Antonius Kettrup (editor) Wiley-VCH Verlag, Weinheim ISBN 3 527 27053 1
- [3] Institut National de Recherche et de Sécurité (2002) Anions Minéraux Fiche Métropol 009 INRS, Vandoeuvre, France <http://www.inrs.fr/metropol>
- [4] British Standards Institution (1994) *Workplace atmospheres — General requirements for the performance of procedures for the measurement of chemical agents* BS EN 482 BSI, London ISBN 0 580 23644 7
- [5] British Standards Institution (2001) *Workplace atmospheres — Measurement of chemical agents present as mixtures of airborne particles and vapour — Requirements and test methods* DD ENV 13936 BSI London ISBN 0 580 38411 X
- [6] British Standards Institution (1995) *Vocabulary of metrology — Part 3: Guide to the expression of uncertainty in measurement* PD 6461: Part 3 BSI, London ISBN 0 580 23482 7
- [7] Health and Safety Executive *Occupational exposure limits Guidance Note EH 40* (updated annually)
- [8] British Standards Institution (1993) *Workplace atmospheres — Size fraction definitions for measurement of airborne particles* BS EN 481 BSI, London ISBN 0 580 22140 7
- [9] Chung K Y K (1998) *Collection efficiencies of sorbent tubes for larger particles* HSL Report IR/A/98/06 Health and Safety Laboratory, Sheffield, England
- [10] Kenny L C *et al* (1997) *A collaborative European study of personal inhalable aerosol sampler performance* Ann Occup Hyg **41** 135-153
- [11] Demange M *et al* (2002) *Field comparison of 37-mm closed-face cassettes and IOM samplers* App Occup and Environ Hyg **17** (3) 200-208
- [12] Jackson C J, Howe A M and Neuberger C (1981) *Sampling and analysis of galvanizing fume* Anal. Proc. **18** 234-237
- [13] Remijn B *et al* (1982) *Zinc chloride, zinc oxide, hydrochloric acid exposure and dental erosion in a zinc galvanizing plant in the Netherlands* Ann Occup Hyg **25** (3) 299-307
- [14] Lamont V *et al* (1989) *Méthode de caractérisation des ambiances de travail en galvanisation à chaud* Cahiers de notes documentaire **134** (1) 87-97, HSE Translation Service *Method for characterising working environments in hot-dip galvanizing* HSE Translation 16523D
- [15] URG Corporation *URG's Personal Sampling Monitors* <http://www.urgcorp.com/catalogs/personalsampleroverview.pdf>
- [16] Thermo Electron Corporation - rp Air Quality Instruments *ChemPass Model 3400 Personal Sampling System* <http://www.rpco.com/products/ambprod/amb3400/index.htm>

[17] Institut National de Recherche et de Sécurité (2003) *Ammoniac et sels d'ammonium*
Fiche Métropol 013 INRS, Vandoeuvre, France <http://www.inrs.fr/metropol>

[18] Ramsey K W (1980) *Galvanizing – A survey of personal exposure to fume* Occupational
Hygiene Section FI 9 Report FISM/9/1980/30