An Analytical Application for the Determination of Metals in PM$_{10}$

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1. Introduction

Air quality standards for Ireland European Council, 2008: Ambient Air Quality and Clean Air for Europe Directive 2008/50/EC [1], require that the annual limit for particulate matter ten microns (PM$_{10}$) per defined agglomeration zone within Ireland has an annual limit of 40 $\mu$gm$^{-3}$, the annual limit for PM$_{2.5}$ from January 1$^{st}$ 2010 is 25 $\mu$gm$^{-3}$. A 24 h PM$_{10}$ mean per defined agglomeration zone of 50 $\mu$gm$^{-3}$ is not to be exceeded more than thirty five times in one year. This directive came into effect in 2010 and has replaced air quality standards European Council, 1999. Air Quality Daughter Directive 1999/30/EC [2], (which) was implemented in 2005 under Air Quality Standard Regulations 2002 S.I. No. 271 of 2002 [3].

Particulate matter ten microns (PM$_{10}$) is the subject of international publicity, particularly with reference to its associated health impacts [4, 5]. Research in the field has varied from the development of analytical applications for the determination of particulate matter and its chemical components, to epidemiological studies, to the impacts of PM on human health. A specific investigation of particulate matter exposure has also presented a link to mortality rates [6]. Epidemiological studies should consider the determination of the metal content in particulate matter due to their potential negative effects upon human health [7].

PM$_{10}$ is classified into two modes; coarse particles and fine particles. Coarse particles arise from such primary sources as the re-suspension of road dust, agricultural activity, sea spray, concrete production and other industrial processes [8]. Fine particles can result from secondary inorganic aerosols and volatile organic compounds, which arise from anthropogenic activity like combustion and traffic emissions [9]. Anthropogenic activities can cause atmospheric chemical reactions and produce such pollutants as nitrous oxides, sulphur dioxide, nitrate and ammonium along with soluble metallic substances like iron and chromium [10]. It has been determined that the calcium portion of particulate matter can be found with sulphate, as calcium sulphate and chloride can be found as sodium chloride [11].

Atmospheric particulate matter is often non spherical with a range of densities [12]. Some particles are liquid, some solid and others have solid cores surrounded by liquid. Particles
may be hygroscopic, contain particle bound water, inorganic ions, metallic compounds and elemental carbon. It is impossible to assess fully all components of PM$_{10}$ due to the significant portion of particle bound water, which may not be completely removed by pre-sample filter conditioning. Furthermore, the removal of particle bound water may result in loss of semi-volatile particulate matter [12]. Studies have shown variable losses of ammonium nitrate at certain temperatures from quartz filters while, the loss of semi-volatile particles can occur during transport and storage of filters [13].

The European Union has designated EN 14902:2005 [14] as the standard method for the analysis of the metallic component of PM$_{10}$ utilising Inductively Coupled Plasma Mass Spectroscopy (ICP-MS) and microwave digestions with nitric acid and hydrogen peroxide extraction. The standard states that, demonstration of validation can determine the equivalency of an alternative test. The limitation of resources by accredited laboratories means that the use of alternative instrumentation as Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) can be used in determining PM$_{10}$ metallic fractions.

For Ireland, the climate is influenced by the Atlantic Ocean with prevailing south westerly-to-westerly winds and little significant variation in temperatures [15]. This research study details the investigation of validation of particulate matter metal analysis and investigates the impact of the metallic portion of PM$_{10}$ levels at a sampling site in County Cork, Ireland in 2005 and examines the impact of source emissions on ambient air quality following EU Directive 1999/30/EC [1]. The study site is located in an area, which includes an industrial zone.

2. Methodology

2.1 Sampling sites

The determination of the PM$_{10}$ fraction of suspended particulate matter was measured following the European reference method EN 12341 European Union 1998 [16]. The site selected is located in an area, which includes an industrial zone with a mineral extraction quarry and asphalt production plant. During the study time period, a landfill was operating within the study site. The road network in the area suffered much wear and tear during the study due to heavy vehicles and machinery utilising the small local access roads. Housing development became more frequent in this area during this time and the site location is also in close proximity to the coast with a large water body near-by with a potential for high sea salt contribution to particulate matter.

2.2 Sampling and measurements

The sampling of atmospheric particulate matter was carried out by means of a ‘TCR TECORA’ PM$_{10}$ Analyser “Sky post PM/HV” sampler equipped with PM$_{10}$ inlet and quartz fibre filters (47mm Schleicher and Schuell). Daily sampling was performed from 18 March to 19 May 2005.

Once gravimetric analysis and filter mass loading had been computed, sample and control filters were digested following the USEPA [17] method described in Byrd et al., (2010) [18]. The solutions obtained were analysed by inductively coupled argon plasma optical emission spectrophotometer. Settings for the ICP-OES are outlined in Table 1.
### Table 1. Instrument characteristics and settings for ICP-OES

| Parameter                              | Setting          |
|----------------------------------------|------------------|
| Forward rf power                       | 1300 W           |
| Frequency of rf generator              | 40 MHz (axial view) |
| Coolant gas flow rate                  | 15 l/min         |
| Auxiliary gas flow rate                | 0.2 l/min        |
| Sample gas flow rate                   | 0.8 l/min        |
| Solution delivery                      | 1.0 ml/min       |
| Automatic sampler                      | Perkin-Elmer AS900 |
| Nebulizer                              | Cross-flow with Scott type expansion chamber |
| Polychromator                          | Echelle grating, cross-dispersed wavelength range (nm): 165–403 |
| Detector                               | Segmented-array charge coupled device |
| Measurement mode                       | Continuous nebulization |
| Signal processing mode                 | 3 pixels peak area |
| Background correction                  | 2 points         |
| Wavelengths (nm)                       |                  |
| Al, 308.215                            |                  |
| Cd, 228.802                            |                  |
| Cr, 267.716                            |                  |
| Cu, 324.742                            |                  |
| Fe, 238.204                            |                  |
| Mn, 257.610                            |                  |
| Ni, 232.003                            |                  |
| Pb, 217.000                            |                  |
| Zn, 206.200                            |                  |
| Ca, 317.949                            |                  |
| K, 404.721                             |                  |
| Na, 330.236                            |                  |
| Mg, 279.075                            |                  |

#### 2.3 Standards and controls

Single and mixed metallic standards are commercially available for use with Inductively Coupled Plasma Spectroscopy (ICP-OES). The National Institute of Standards and Technology (NIST) standard reference materials for calibration (1 – 30 µg/ml) were prepared in dilute digestion acid solution. Validation parameters were assessed [19] using these standards. Control samples were also used to determine detection limits. Control samples were pre-conditioned quartz fibre filters and these were placed in the PM$_{10}$ Analyser “Sky post PM/HV”, but not exposed to ambient air.

#### 3. Validation

Low volume daily PM$_{10}$ sampling involves the exposure of quartz fibre filters to a known quantity of ambient air over a twenty four hour period in which each filter paper exposed and collected represents one daily sample. Some sample collection equipment provides for multiple samples per day, which is useful when attempting to determine the impact of local activity at various times. However, each individual sample filter is different in composition from the next, as it represents a different time period. Splitting a sample is not possible, as material will not necessarily collect on the filter in a uniform manner [20, 21]; therefore it is necessary to use the complete filter in the treatment process for chemical characterisation. The extraction of quartz fibre filters results in the total destruction of the filter and so the performance of a series of standard additions to a single paper is not possible. The solution to this was to add NIST certified reference standard to blank filters which have undergone the entire sample conditioning process. Calibration and validation of this methodology was performed in this way. The sample matrix changed as the test progressed with a solid filter being incurred with a known concentration of liquid analyte before conditioning and extraction of analyte to a complex liquid matrix. Standard addition of mixed heavy metals in nitric acid was performed. The final volume of standard was 20ml.
Determination of method performance parameters was carried out through revision of expected analyte concentrations in a PM$_{10}$ sample. Limits of Detection (LOD) and limits of Quantitation (LOQ) were assessed through the use of blank filters in accordance with IUPAC rules. From the series of standards devised, the lowest standard took account of blank concentrations and instrumentation sensitivity and was used in the determination of linearity where possible. Blank materials used in the determination of trace metal analysis all contain some level of analyte of interest in the form of contamination. These materials were used to establish a baseline concentration level and results obtained were subtracted from standards and sample values.

The impact of interference is worth considering prior to sample collection. Positive and negative interference can result during transportation of samples to the laboratory; loss of semi-volatile components represents the main volume of such losses through the loss of ammonium nitrate. The loss of particle bound water can result in significant deterioration of PM$_{10}$ sample concentration [22]. Conditioning of filters by humidification standardises the preparation of the test filter so as to ensure traceability and accuracy of the complete analytical process.

3.1 Filter paper humidification assessment

A critical step in the process is the conditioning of filter papers at a stable low relative humidity. Variable humidity causes changes in the size of hygroscopic particles. This results in the loss of volatile ammonium nitrate and semi volatile organic components by evaporation [12]. This step in the procedure was developed to determine its influence upon analyte recovery. First, a standard addition series was devised (Table 2). Each standard contained a mixture of all elements to be analysed.

Second, a batch of blank filter papers was prepared by spiking a mixture of standards of decreasing concentration (Table 2). This batch consisted of 6x10 filter papers. The standard elemental mix was incurred onto 10 filter papers over 6 standard concentrations [Table 2]. This batch of filter papers was subjected to the full procedure described in Byrd et al., 2010 [18] including the treatment of filter papers before standards were added and the treatment

| Element | Blank | Std 1 | Std 2 | Std 3 | Std 4 | Std 5 |
|---------|-------|-------|-------|-------|-------|-------|
| Al      | 0     | 0.05  | 0.2   | 0.5   | 1     | 1.5   |
| Ba      | 0     | 0.05  | 0.2   | 0.5   | 1     | 1.5   |
| Cd      | 0     | 0.05  | 0.2   | 0.5   | 1     | 1.5   |
| Co      | 0     | 0.05  | 0.2   | 0.5   | 1     | 1.5   |
| Cr      | 0     | 0.05  | 0.2   | 0.5   | 1     | 1.5   |
| Cu      | 0     | 0.05  | 0.2   | 0.5   | 1     | 1.5   |
| Fe      | 0     | 0.05  | 0.2   | 0.5   | 1     | 1.5   |
| Mn      | 0     | 0.05  | 0.2   | 0.5   | 1     | 1.5   |
| Ni      | 0     | 0.05  | 0.2   | 0.5   | 1     | 1.5   |
| Pb      | 0     | 0.05  | 0.2   | 0.5   | 1     | 1.5   |
| Zn      | 0     | 0.05  | 0.2   | 0.5   | 1     | 1.5   |
| Ca      | 0     | 1     | 5     | 10    | 50    | 100   |
| Mg      | 0     | 5     | 2.5   | 5     | 25    | 50    |
| K       | 0     | 0.1   | 0.5   | 1     | 5     | 10    |
| Na      | 0     | 0.5   | 2.5   | 5     | 25    | 50    |

Table 2. Elements and standard concentrations (μg/ml) applied to filter papers during validation studies.
of filter papers after the standard was added in a desiccator at fixed relative humidity and
temperature [Humidification study: Batch A]. A second batch of blank filter papers was
prepared consisting of 6x10 filter papers. These filters were treated in the same way as the
filters in batch A without desiccating after standard addition [Non-humidification study:
Batch B]. Spiked filter papers for both batches were weighed using a semi-micro balance
prior to and following conditioning.

3.2 ICP-OES validation results

Average concentrations (n=10) for blank filters in Batches A and B were determined. These
results were used to determine performance characteristics such as LOD and LOQ (Table 3
and 4). Limit of detection is derived from the standard deviation of the mean blank result
obtained. LOD is the lowest concentration of analyte that can be detected and reliably
distinguished from zero [23]. LOD can be expressed as:

\[ \text{LOD} = Y_{\text{blank}} + 3s_{\text{blank}} \]  

where \( Y_{\text{blank}} \) is the average value of the blank signal and \( s_{\text{blank}} \) is the corresponding standard
deviation of that average blank signal. Limit of Quantitation is the lowest concentration of
analyte that can be determined quantitatively with an acceptable level of precision [23].
LOQ can be expressed as:

\[ \text{LOQ} = Y_{\text{blank}} + 10s_{\text{blank}} \]  

LOD values for humidified filters (Batch A) of Al, Ba, Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb, Zn
ranged from 0.001-0.038 µg/ml, LOQ ranged from 0.008-0.21 µg/ml (Table 3). LOD values
for Ca, Mg, K, and Na ranged from 0.06-1.81 µg/ml with the LOQ ranging from 0.32-1.32
µg/ml (Table 3). LOD values for non-humidified filters (Batch B) of Al, Ba, Cd, Cr, Co, Cu,
Fe, Mn, Ni, Pb, and Zn ranged from 0.001-0.056 µg/ml with the LOQ ranging from 0.008-
0.31 µg/ml (Table 4). LOD values for Ca, Mg, K, and Na ranged from 0.003-3.91 µg/ml and
the LOQ ranged from 0.18-21.41 µg/ml (Table 4).

The elements Ba, Cu, Fe, Mn, Ni, K and Na all presented favourable LOD and LOQ values
for Batch A compared with Batch B. Further comparison of the data presented (Table 3 and
4) shows that LOD, LOQ and average value of blank signal for the elements Al, Cr, Zn, Ca
and Mg are of greater concentration on those filters that have been humidified as part of the
conditioning treatment process. This can be attributed to the impact of the desiccant on the
humidification process and on the impurities in the digestion acid mixture. This presents a
challenge to the linearity range obtainable for those elements, which inevitably will have
higher LOQ values.

LOD and LOQ values obtained for cobalt in those filter papers that have been humidified
(Batch A) was 0 µg/ml. This is because the standard deviation of these 10 filters was 2.25.x10-19 µg/ml.

In filters that have been humidified (Batch A), Al and Fe had LOQ values greater than the
lowest standard concentration used (0.05 µg/ml). The linear range of these elements
therefore does not include this standard.

In Batch A (Table 5), accepted relative standard deviation values (%RSD) ranged from 0.9-
15.1% (Limit <20%) with acceptable recovery values ranging from 80.3-118.8% (Limits 80-
120%). These results correlate with the precision values obtained (Table 5). There are some
| Element | Humidification Process (Batch A) | Non-Humidification Process (Batch B) |
|---------|----------------------------------|--------------------------------------|
|         | Mean LOD soln LOD air LOQ soln LOQ air IDL soln IDL air | Mean LOD soln LOD air LOQ soln LOQ air IDL soln IDL air |
|         | ng/m³ µg/ml ng/m³ µg/ml ng/m³ µg/ml | ng/m³ µg/ml ng/m³ µg/ml ng/m³ µg/ml |
| Al      | 23.4 0.014 11.75 0.077 64.15 0.008 6.42 | 15.83 0.004 3.73 0.025 20.83 0.003 2.08 |
| Ba      | 5.3 0.005 4.00 0.026 21.66 0.003 2.17 | 4.42 0.005 4.09 0.027 22.50 0.003 2.25 |
| Cd      | 0.65 0.001 1.21 0.008 6.67 0.001 0.67 | 0.58 0.001 1.21 0.008 6.67 0.001 0.67 |
| Co      | 0.83 0.000 0.00 0.00 0.00 0.00 0.00 | 0.58 0.001 1.21 0.008 6.67 0.001 0.67 |
| Cr      | 4.67 0.004 3.25 0.021 17.50 0.002 1.75 | 2.58 0.002 1.84 0.012 10.00 0.001 1.00 |
| Cu      | 1.92 0.002 1.25 0.008 6.67 0.001 0.67 | 2.25 0.004 3.34 0.022 18.33 0.002 1.83 |
| Fe      | 50.32 0.038 31.49 0.207 172.47 0.021 17.25 | 60.82 0.056 46.70 0.307 255.78 0.031 25.58 |
| Mn      | 1.08 0.002 1.25 0.008 6.67 0.001 0.67 | 1.17 0.002 1.29 0.009 7.50 0.001 0.75 |
| Ni      | 3.33 0.004 3.25 0.021 17.50 0.002 1.75 | 3.08 0.005 3.92 0.026 21.66 0.003 2.17 |
| Pb      | 1.82 0.007 6.17 0.041 34.16 0.004 3.42 | 1.79 0.007 6.17 0.041 34.16 0.004 3.42 |
| Zn      | 23.66 0.017 14.00 0.093 77.48 0.009 7.75 | 33.58 0.070 58.24 0.383 319.10 0.038 31.91 |
| Ca      | 230.87 0.240 199.96 1.316 1096.45 0.132 109.64 | 139.56 0.145 120.48 0.794 661.53 0.079 66.15 |
| K       | 17.5 0.058 47.99 0.316 263.28 0.032 26.33 | 42.08 0.075 62.08 0.409 340.77 0.041 34.08 |
| Mg      | 33.58 0.070 58.24 0.383 319.10 0.038 31.91 | 33.58 0.003 2.65 0.175 145.80 0.018 14.58 |
| Na      | 1560.5 1.810 1507.70 0.992 826.50 0.099 82.65 | 1780.98 3.905 3253.43 21.411 17838.93 2.141 1783.89 |

Table 3. Average concentrations (n=10) for blank filters in Batch A (Humidified) with limits of detection, limits of quantitation and instrument detection limits reported.

Table 4. Average concentrations (n=10) for blank filters in Batch B (Non-humidified) with limits of detection, limits of quantitation and instrument detection limits reported.
### Table 5. Batch A. Filters have been conditioned at constant relative humidity and temperature following addition of standard and prior to analysis by ICP-OES. Bold values represent outliers.

exceptions in the relative standard deviation values and recovery values obtained. The lowest standard (0.05 μg/ml) for Al, Zn and Fe displayed relative standard deviations greater than 20%. On further examination, the precision values obtained for Al and Zn show that there is no significant deviation from the true value of this standard when compared with other standards. The reason for these high %RSD values is that at such a low concentration, a slight variation has a big impact upon relative standard deviation. In the case of Fe, the mean concentration value obtained for this standard is a half of the true value spiked on the filter. The LOQ value for Fe (Table 3) is greater than the 0.05 μg/ml spiked standard. The recovery values for Cd, Cr and Pb in standard one (0.05 μg/ml) are greater than the upper percentage limit of 120% (Table 5). The average values obtained for these standards are greater than the true concentration. There is a positive bias observed in these standards (Table 5). With reference to Ca, Na, Mg and K; Na (0.5, 2.5 μg/ml) presented no elemental reading due to instrument sensitivity constraints. The result for standard 5 μg/ml is that the recovery value is less than the 80% limit (Table 5). These results can be attributed to the high LOQ obtained for these elements.

Ca (1.0 μg/ml) and K (0.1 μg/ml) also presented recovery values less than the lower limit for recovery (Table 5). These results can be attributed to the high LOQ obtained for these elements.
elements (Table 3). For Mg, all standards are within the required limits for relative standard deviations and recovery.

In Batch B (Table 6), acceptable relative standard deviation values (%RSD) range from 0.876-18.527% (Limit <20%). Acceptable recovery values range from 80.1-119.9% (Limits 80-120%), (Table 6). However, the following standards: Al, Fe (0.05 μg/ml), present relative standard deviation values above the limit of 20% RSD. On further evaluation, recovery values (Table 6) for the elements Al and Fe are less than the lower limit for recovery of 80%.

These values can be attributed to the loss of particle bound water from the standards due to the lack of humidity and temperature control. The elements Na, Ca and K at concentrations Na (0.5, 2.5, 5.0 μg/ml), Mg (0.5, 2.5 μg/ml), Ca (1.0, 5 μg/ml), K (0.1, 0.5 μg/ml) gave no detectable reading (Table 6). These results can be attributed to the high LOQ results obtained for these elements (Table 4).

Table 6. Batch B. Filters have not been conditioned at constant relative humidity and temperature following addition of standard and prior to analysis by ICP-OES. Bold values represent outliers.
A linearity study was conducted on Batch A (Humidification). Good linearity was obtained across the accepted ranges (Table 7). High limit of quantitation values (LOQ), which led to poor recovery values for elements at certain low standard concentrations have already been discussed. For this reason the linear range of some elements was reduced. The Pearson coefficient ($R^2$) was calculated for each element for those filters that were humidified (Batch A) (Table 7). $R^2$ ranges from 0.997-0.999.

| Element | Equation of the Line | Linear Range | $R^2$ | P-Value |
|---------|----------------------|--------------|-------|---------|
| Al      | $y=0.8528x+0.0149$   | 0.05-1.5     | 0.9992| 0.824   |
| Ba      | $y=0.8502x+0.0297$   | 0.05-1.5     | 0.9983| 0.852   |
| Cd      | $y=0.8831x+0.0283$   | 0.05-1.5     | 0.9985| 0.8968  |
| Co      | $y=0.8807x+0.0269$   | 0.05-1.5     | 0.999 | 0.8906  |
| Cr      | $y=0.8725x+0.211$    | 0.05-1.5     | 0.986 | 0.8662  |
| Cu      | $y=0.8649x+0.0257$   | 0.05-1.5     | 0.981 | 0.8649  |
| Fe      | $y=0.8566x+0.0106$   | 0.2-1.5      | 0.995 | 0.7913  |
| Mn      | $y=0.8727x+0.0265$   | 0.05-1.5     | 0.981 | 0.878   |
| Ni      | $y=0.8662x+0.0228$   | 0.05-1.5     | 0.985 | 0.8606  |
| Pb      | $y=0.883x+0.0331$    | 0.05-1.5     | 0.992 | 0.907   |
| Zn      | $y=0.8948x+0.0204$   | 0.05-1.5     | 0.975 | 0.8971  |
| Ca      | $y=1.0586x-0.7582$   | 5-100        | 0.9996| 0.9604  |
| K       | $y=1.0406x-0.175$    | 0.5-10       | 0.989 | 0.9982  |
| Mg      | $y=1.0408x-0.2198$   | 0.5-50       | 0.9999| 0.9765  |
| Na      | $y=1.02x-1.3319$     | 5.0-50       | 0.999 | 0.9678  |

Table 7. Batch A. Regression statistics assigned to standards from ANOVA analysis.

The values are acceptable considering the matrix involved and the impact of the conditioning process (Fig. 1). The data was analysed by ANOVA. The $p$ values obtained show insignificant statistical variation within the linear ranges (Table 7). The linear range for the elements Al, Ba, Cd, Co, Cr, Cu, Mn, Ni, Pb, and Zn are 0.05-1.5 µg/ml. For Fe, the linear range was 0.2-1.5 µg/ml, Ca 5-10 µg/ml, K 0.5-10 µg/ml, Mg 0.5-50 µg/ml and Na 5-50 µg/ml. Repeat analysis of Batch A was performed at a time delay of three days after the initial analysis. In all elements analysed, the lowest standard (0.05 µg/ml) did not produce an elemental reading. Furthermore, standards Al (0.2, 1.0 µg/ml) Cr (0.2 µg/ml), Fe (0.2 µg/ml) presented recovery values less than the lower recovery limit of 80% (Table 8). This can be attributed to the deterioration of standards over time following digestion. Therefore, analysis should be performed immediately following digestive treatment of filter papers.
Fig. 1. Overlay of the standard calibration curves (µg/ml) against the actual recorded ICP readings for the elements from sample filters (n=39; blue diamond symbol). Curve A represents Aluminium, with a linear regression of $R^2=0.9956$ for spiked standards; Curve B: Iron, $R^2=0.9973$; Curve C: Calcium, $R^2=0.9996$; Curve D: Copper, $R^2=0.9986$. 
Table 8. Batch A. repeat analysis to determine stability of filters which have been conditioned at constant relative humidity and temperature following addition of standard and prior to analysis by ICP-OES. Bold values indicate outliers.
Significance testing was performed on Batch A against Batch B to determine the statistical significance of the removal of the conditioning step in Batch B. A test was also applied to data from batch A and the repeat analysis of Batch A to determine the statistical significance of delay in analysis following digestion.

Significant statistical differences were observed between Batch A repeat (N=2) (Table 9). This was expected due to the deterioration of standards as previously discussed. No statistical differences were observed between Batch A and Batch B (Table 9). This was despite the fact that poor recovery values were obtained in Batch B.

| Element | Batch Compared | F-Values | Standard Conc. µg/ml | Fcrit |
|---------|----------------|----------|----------------------|-------|
|         |                 |          | 0.05 0.2 0.5 1 1.5    |       |
| Al      | A1 vs A2       | 0.3434   | 0.2342 1.8520 1.8182 0.7384 |       |
|         | A1 vs B1       | 0.3286   | 0.1063 0.1571 0.5140 0.9969 1.0358 |       |
| Cu      | A1 vs A2       | **4.8889** | **5.9221** 1.9381 1.6138 2.2133 |       |
|         | A1 vs B1       | 0.6418   | 1.6438 0.9650 0.7862 0.5859 0.8649 |       |
| Fe      | A1 vs A2       | 0.2544   | 2.6744 1.1611 2.1950 4.2165 |       |
|         | A1 vs B1       | 0.8155   | 0.0001 0.1629 0.7884 1.1858 0.3047 |       |
| Mn      | A1 vs A2       | 2.1523   | 0.6792 1.5032 1.2188 3.0147 |       |
|         | A1 vs B1       | 0.9111   | 0.9714 1.1028 1.0376 0.7959 0.3581 |       |
| Ni      | A1 vs A2       | 0.6221   | 0.6958 2.9769 1.0100 2.4429 |       |
|         | A1 vs B1       | 1.2095   | 1.6625 0.9714 0.4916 1.2891 0.3237 |       |
| Pb      | A1 vs A2       | 0.8889   | 1.2557 2.6848 1.9018 0.0196 |       |
|         | A1 vs B1       | 0.6162   | 2.1552 0.5370 0.4081 1.2534 0.5629 |       |
| Ba      | A1 vs A2       | **93.4444** | **7.6962** 2.6462 **5.1197** |       |
|         | A1 vs B1       | 2.4873   | 1.5556 0.4276 0.6406 0.8042 0.3436 |       |
| Zn      | A1 vs A2       | **143.8148** | 0.2590 0.4886 0.5395 0.0104 |       |
|         | A1 vs B1       | 0.8896   | 1.2818 1.6404 0.8925 0.4590 0.2799 |       |

Table 9. Results of significance testing of Humidified filters (Batch A) versus Humidified filters repeat analysis (Batch A Repeat) and Humidified filters (Batch A) versus Non-Humidified filters (Batch B). Bold values indicate significant statistical differences.

4. Case study

In the spring-summer of 2005 fifty-nine daily samples were taken and thirty-nine of these daily samples were analysed for metals by ICP-OES. Average daily PM$_{10}$ values were 34 µgm$^{-3}$, with a high value of 89 µgm$^{-3}$ PM$_{10}$ (Table 10). Metal values displayed (Table 10),
show the constituent portions for each element on the day this maximum value was observed. The median PM$_{10}$ value observed for the period was 29 µgm$^{-3}$ (Table 10). Wind speed was a significant contributor to high particulates when coupled with low precipitation, particularly when the weather system was originating in the Atlantic Ocean.

| Monitoring Period | Type          | Samples | PM$_{10}$ | Al     | Fe   | Ca   | K    | Mg | Na | Pb | Zn | Cu | Mn |
|-------------------|---------------|---------|-----------|--------|------|------|------|----|----|----|----|----|----|
|                   | Total Filters | µgm$^{-3}$ | ngm$^{-3}$ | µgm$^{-3}$ | µgm$^{-3}$ | µgm$^{-3}$ | µgm$^{-3}$ | ngm$^{-3}$ | ngm$^{-3}$ | ngm$^{-3}$ | ngm$^{-3}$ | ngm$^{-3}$ | ngm$^{-3}$ |
| Spring-Summer 2005| Mean          | 59      | 34        | 82     | 147  | 9.9  | 185  | 164 | 0.124 | 9   | 72  | 5  | 14 |
|                   | Max Daily     | 89      | 299       | 471    | 24.5 | 604  | 646  | 2.18 | 22   | 146 | 31 | 31 |
|                   | Max Daily %   | 0.46    | 0.72      | 27.84  | 1.31 | 0.71 | 5.89 | 0.04 | 0.32  | 0.04 | 0.03 |    |
|                   | Max Daily PM$_{10}$ | 65     | 65       | 88     | 46   | 65   | 37   | 49  | 45   | 65  | 89 |
|                   | Median        | 29      | 65        | 92     | 8.4  | 167  | 124  | 0   | 8    | 68  | 2  | 11 |
|                   | Mean %        | 0.24    | 0.43      | 29.12  | 0.54 | 0.48 | 0.36 | 0.03 | 0.21  | 0.02 | 0.04 |    |

Table 10. Collection Site PM$_{10}$ data and selected chemical analysis results

Back trajectories arriving at this observation site were obtained from the web version of the Hybrid Single Particle Langrangian Integrated Trajectory (HYSPLIT) model [24] from March 15$^{th}$ to May 22$^{nd}$ 2005 (Fig. 2 and 3). NOAA’s Air Resources Laboratory (ARL) archives were used to establish back trajectories [25]. These back trajectories show the air mass over the observation site during the study period. Air mass was primarily emanating from a west-south westerly direction during the study period bringing Atlantic Air. This air mass is associated with higher wind speed causing the increase in concentration of coarse particulate matter (2.5-10 µm) due to earth crust and sea-salt sources [26]. Brief periods also prevailed when the air mass originated from the United Kingdom (Fig. 2 C), Northern European countries such as Poland (Fig. 2 D) and the Arctic regions (Fig. 3 A). This air mass is associated with anthropogenic pollutants and is considered part of the fine particulate matter fraction (0-2.5 µm) [15].

### 4.1 Principal component analysis

Principle Component Analysis (PCA) was applied to data using STATISTICA software (StatSoft, Tulsa, OK, USA) upon those samples obtained which exceeded the daily PM$_{10}$ limit of 50 µgm$^{-3}$. The most related groups were (Mg$^{2+}$, Zn$^{2+}$, Cu$^+$, Ca$^{2+}$), (Al$^+$, Mn$^+$, Fe$^{2+}$), (K$^+$, Pb$^{2+}$).

VARIMAX rotation of the data presents three factors that were observed to be associated with particulate matter concentrations during these daily exceedances accounting for 84.3% of total variation (Table 11). The first factor has a high loading for Cu$^+$, Ca$^{2+}$, Mg$^{2+}$ whilst also observing significant loading of Zn$^+$ (Table 11) and identifies crustal material and road dust re-suspension as the source [26]. During the study period, local access roads in the area were in need of repair. The influence of heavy industrial traffic upon these roads was significant. The high concentration of quarrying extractive industry in the area led to much deposition of dust along access roads, which was re-suspended on days of high wind speed, leading to an increase in the concentration of particulate matter. The second factor presented high loading for Al$^+$, Mn$^+$ and Fe$^{2+}$ associated with traffic with extractive industry in the area (Table 11). Na$^+$ was not found to be present in any of the samples, which exceeded the daily limits and therefore could not have a principal component analysis applied to it in this case. The third factor is indicative of differing types of industrial activity in the locality. K and Pb$^{2+}$ are indicative of industrial factors [27].
Fig. 2. Back trajectories of air mass flow over the observation site during study period obtained from NOAA HYSPLIT web based model; (A) March 15th 2005; (B) March 22nd 2005; (C) March 29th 2005; (D) April 8th 2005.
Fig. 3. Back trajectories of air mass flow over the observation site during study period obtained from NOAA HYSPLIT web based model; (A) April 15th 2005; (B) April 22nd 2005; (C) April 29th 2005; (D) May 22nd 2005.
Table 1. Principal Component Factor analysis on PM$_{10}$ element concentration data set. Bold values represent strong correlation to specific factors.

Principal Component plots (95% confidence level) indicate a strong correlation of elements associated with coarse particles (2.5-10 µm) and PM$_{10}$ concentration values obtained. Al (r=0.6717) and Fe (r=0.741) are traffic in origin and Mg (r=0.59) is associated with high wind speed causing the re-suspension of road dust (Fig. 4 A, C, D). Ca (r=0.399) is associated with crustal origin and the re-suspension of road dust, though does not correlate as strongly with particulate matter concentration (Fig. 4. B). K (r=0.37) is associated with industrial combustion (Fig. 5. C). Mn (r=0.49) in this case is associated with traffic sources (Fig. 5. A). Cu (r=0.054) and Zn (r=0.046) are associated with wear and tear from tyres of vehicles. These elements display no correlation with PM$_{10}$ concentration during the study (Fig. 5. B, D).

Principal component scatter plots were used to determine the correlation between PM$_{10}$ and its constituent elements in a study in Argentina [21] with significant correlations highlighted and discussed.

4.2 Enrichment factors

The anthropogenic contribution to the elemental composition of PM$_{10}$ in samples, which exceeded the daily limit of 50 µgm$^{-3}$ was assessed by calculation of Enrichment Factor (EF) for each element using Al as a reference, utilising the crustal composition equation as given by Mason and Moore 1966 [28].

$$EF_{Al}(X) = \frac{(X/Al)_{air}}{(X/Al)_{crust}}$$

Enrichment factors (Fig. 6) show Fe, K, Mg <10 EF attributable to natural sources. Fe is assigned to traffic factor, Mg is assigned to re-suspension of road dust and K, assigned to an
industrial factor is attributable to heavy extractive industry in the area. Ca and Cu show slightly enriched levels correlating with the crustal material factor assigned under PCA. Mn, Pb and Zn are all enriched to an elevated level. Zn and Mn are assigned to traffic factor; Pb is assigned to industrial activity.

A; $PM_{10}$ $\mu g/m^3$ vs. Al ngm$^{-3}$; $Al = -16.16 + 0.00187 \times PM_{10}$; Correlation: $r = 0.67167$; 0.95, Confidence Interval
B; $PM_{10}$ $\mu g/m^3$ vs. Ca ngm$^{-3}$; $Ca = 6754.5 + 0.08292 \times PM_{10}$; Correlation: $r = 0.39914$; 0.95, Confidence Interval
C; $PM_{10}$ $\mu g/m^3$ vs. Fe ngm$^{-3}$; $Fe = -56.61 + 0.00393 \times PM_{10}$; Correlation: $r = 0.74102$; 0.95, Confidence Interval
D; $PM_{10}$ $\mu g/m^3$ vs. Mg ngm$^{-3}$; $Mg = -1.679 + 0.00306 \times PM_{10}$; Correlation: $r = 0.58740$; 0.95, Confidence Interval

Fig. 4. Correlation of $PM_{10}$ concentration versus concentration of individual metallic elements as a constituent component of particulate matter for the assessment site. $PM_{10}$ Concentration as the line graph while elemental readings are illustrated as points.
A; PM$_{10}$ µg m$^{-3}$ vs. Mn ng m$^{-3}$; Mg = 9.1546 + 0.00010 * PM$_{10}$; Correlation: r = 0.37044; 0.95, Confidence Interval
B; PM$_{10}$ µg m$^{-3}$ vs. Cu ng m$^{-3}$; Cu = 4.4761 + 0.00001 * PM$_{10}$; Correlation: r = 0.05387; 0.95, Confidence Interval
C; PM$_{10}$ µg m$^{-3}$ vs. K ng m$^{-3}$; K = 12.317 + 0.00321 * PM$_{10}$; Correlation: r = 0.48838; 0.95, Confidence Interval
D; PM$_{10}$ µg m$^{-3}$ vs. Zn ng m$^{-3}$; Zn = 72.388 - 0.0001 * PM$_{10}$; Correlation: r = -0.0459; 0.95, Confidence Interval

Fig. 5. Correlation of PM$_{10}$ concentration versus concentration of individual metallic elements as a constituent component of particulate matter for the assessment site. PM$_{10}$ Concentration as the line graph while elemental readings are illustrated as points.
5. Comparative study

Other validation studies of the elemental composition of PM$_{10}$ have been presented with the goal of achieving a validated, robust working method for the analysis of particulate matter. The use of extractive techniques is commonplace with various extractive materials used [29]. Extractive material used will depend upon the instrumentation involved, in order to present the analyte in the appropriate form for analysis.

In this study, blank filter papers were used for the determination of the average value of blank signal (n=10). Standard deviations from these blank filters were used to determine LOD and LOQ values [21]. The average concentration of blank values, were presented in a specific study ranging from 1.6-40 ngm$^{-3}$ [20]. Comparable results 1.92-50 ngm$^{-3}$, were obtained in this study (Table 3). LOD values in this study, not including those elements previously mentioned as having some level of interference, are comparable with previous similar studies [30]. Previous studies presented LOQ values ranging from 0.97-124 μg$l^{-1}$ [7]. Our values present favourably, ranging from 0.008-1.32 μg/ml. The differences in this case are due to the sensitivity of the instrument used in each study and the differing matrices involved.

Determination of the percentage recovery of analyte is expressed in the majority of studies [7, 21, 31] involving the validation of methodologies. Acceptable recovery values in this study 80.3-118.8% (Table 5) are a good expression of extraction efficiency. These results are comparable with other recovery studies undertaken [21, 31]. At low standard concentration levels, certain elements in our study (Fe, Zn, K, Na) produced poor recovery values attributable to LOQ values greater then the concentrations applied in those standards. A previous validation study highlighted poor recovery for Al, Fe and Zn, which were assigned...
to metal oxides and interference from filter holders [31]. Linearity studies undertaken have presented ranges of $R^2 0.62-1.0$ [32] and $R^2 0.965-0.996$ [7]. In this study, linearity is comparable across the accepted linear range, $R^2$ ranged from 0.986-0.999.

### 6. Conclusion

The determination of the metallic components of PM$_{10}$ by Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) is confirmed to be suitable for application on individual ambient air samples with good analytical performance. Limits of Detection (LOD); 0.001-0.038 μg/ml equivalent to (1.21 - 31.49 ngm$^{-3}$) for heavy metals and 0.06-1.81 μg/ml equivalent to (47.99 – 1507.7 ngm$^{-3}$) for Na, Ca, K, Mg. Limits of Quantitation (LOQ) ranged from 0.008-0.21 μg/ml for heavy metals and 0.32-1.32 μg/ml for Na, Ca, K, Mg. These results are considered satisfactory. % RSD ranged from 0.9-15.1%, while recoveries were 80.3-122.0% for the majority of elements, with exceptions highlighted in the study. The accepted linear range for the method of analysis was established with good Pearson coefficient values ($R^2$ 0.986-0.999) obtained. Precision and trueness values were also established in the validation study.

The validation study gives information on the effects of the conditioning process upon filter papers, standards and samples and provides information on the limitations involved with the determination of certain metals at low concentrations. The conditioning study also confirms that the requirement for the humidification of filter papers is necessary to ensure the loss of analyte due to particle bound water is minimised. Assessment of filter papers not subjected to the humidification step in the procedure presents LOD values 0.001-0.056 μg/ml equivalent to (1.21-46.7 ngm$^{-3}$) for heavy metals, LOQ 0.008-0.31 μg/ml and 0.003-3.91 μg/ml equivalent to (2.65-3253 ngm$^{-3}$) for Na, Ca, K, Mg. LOQ 0.18-21.41 μg/ml. Acceptable % RSD are 0.88-18.5%. Recovery values ranged between 23.6 and 19.9%.

This paper also provides information about the nature and composition of particulate matter in samples where the daily limit for PM$_{10}$ of 50 μgm$^{-3}$ was exceeded. Principal component analysis (PCA) on these results shows the most related groups were (Mg$^{2+}$, Zn$^{2+}$, Cu$^{2+}$, Ca$^{2+}$), (Al$^{3+}$, Mn$^{2+}$, Fe$^{2+}$), (K$^+$, Pb$^{2+}$). VARIMAX rotation presents three associated factors (traffic, road dust and crustal material, industrial) accounting for 84% of total variation. The Atlantic air mass has a major influence on Ireland with high wind speed causing the re-suspension of road dust. Anthropogenic influences may be local in origin or due to the influence of air masses originating over Northern or Central Europe. Principal component plots were presented showing the correlation between particulate matter concentration and individual constituent elements. Enrichment factors calculated for the data set indicate primary sources were the significant influence over particulate matter concentrations.

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