



**Sulphur Dioxide Diffusion Tube Monitoring
Best Practice Guidance
December 2011
Open File Report - 11 - 03
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Introduction

The monitoring of sulphur dioxide (SO₂) has been undertaken by the Montserrat Volcano Observatory (MVO) since 1997. This Best Practice Guidance is designed to provide a thorough reference point for the diffusion tube monitoring that is undertaken by MVO. It employs best practice methods as outlined in the Diffusion Tubes for Ambient NO₂ Monitoring: Practical Guidance for Laboratories and Users produced by AEA Energy and Environment for the Department of Environment, Food and Rural Affairs, UK. Although this Defra practical guidance is in relation to NO₂ diffusion tubes, the same methods of deployment and analysis are relevant for SO₂ monitoring.

The diffusion tubes are referred to as passive samplers which monitor concentrations directly by absorbing the particular pollutant from the surrounding area. SO₂ diffusion tubes can be used to compare to longer averaging air quality objectives such as a year, however, cannot be used to compare to those based on shorter averaging periods such as an hour. They can highlight areas of high concentrations and can be used as a screening exercise but, cannot identify short-term fluctuation in concentrations as a result of wind flows etc.

Storage and Exposure of SO₂ diffusion tubes.

The diffusion tubes are currently supplied by Gradko Environmental on an annual contract (this will need to be renewed around February/March time each year). Contact details for Gradko are:

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Gradko International Ltd
St Martins House
77 Wales Street
WINCHESTER
Hants.
SO23 0RH
UK
Tel: +44 1962 860331
Fax: +44 1962 841339

E-mail: janet@gradko.co.uk/sales@gradko.com

Two batches of tubes are sent by Gradko each time and should arrive within 1-2 weeks that they are due to go out in the field, if there are not here within 10 days of the changeover day contact Gradko to check they have been sent and to get the tracking number. DHL are used as the carrier agent for the diffusion tubes. Diffusion tubes that are in anyway damaged for example the end caps are split or the mesh is damaged should not be used. If this occurs a note should be made as to which location will be subsequently missing a tube.

The diffusion tubes should be exposed and analysed within 12 weeks of their preparation date (preparation date stated on label of diffusion tube batch). They should be stored in a cool dark area

when not being exposed, where there will be no fluctuation in temperature, ideally they should be placed in a refrigerator.

The tubes should be mounted vertically in an area of unrestricted air circulation; with no structures or vegetation overhanging or in the proximity of the tubes. The correct and incorrect positioning of the diffusion tubes can be seen in Figure 1. They should also be located more than 10m from heater flues, air conditioning outlets, extractor fans and underground ventilation shafts. Tubes should be placed no higher than 5m above ground level.

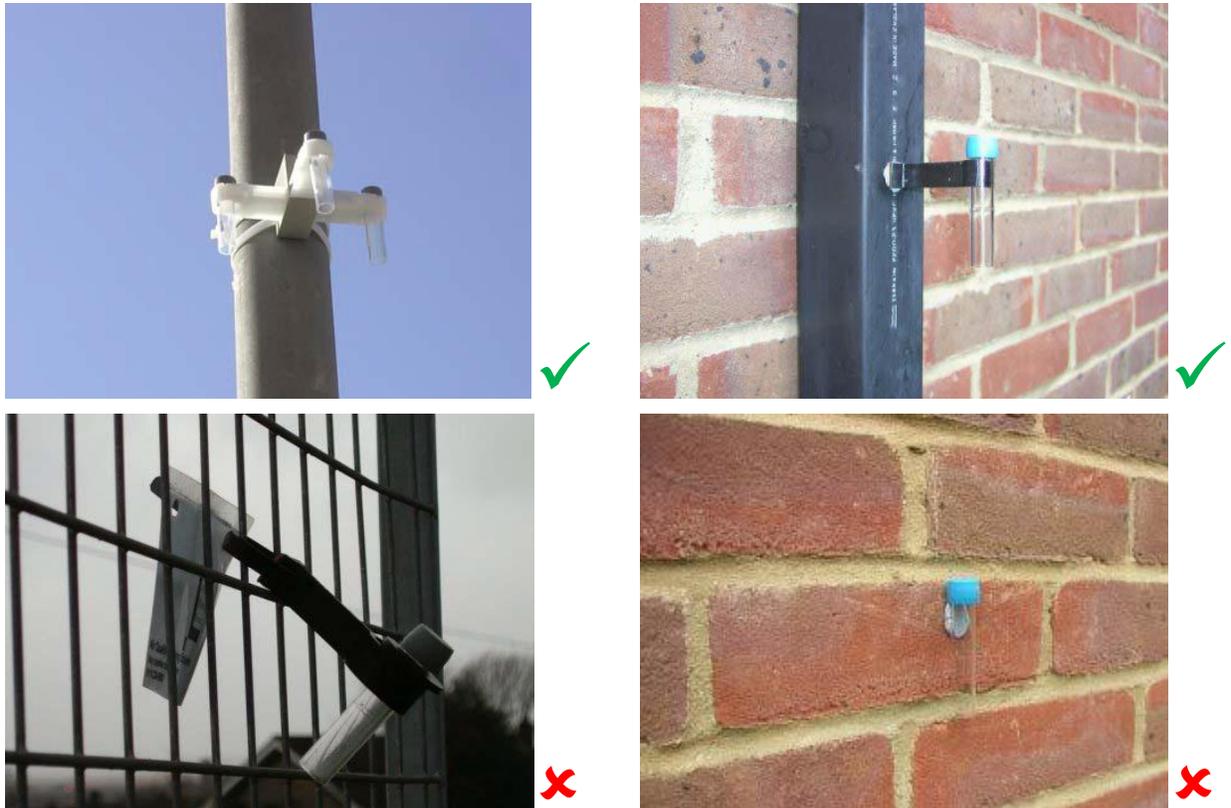


Figure 1 Correct and in-correct positioning of diffusion tubes (Targa *et al.* 2008).

The recommended exposure time for the diffusion tube is 1-4 weeks (Gradko Environmental). When placing the tubes in the field or collecting them in, the date and time should be noted to the nearest 15 minutes. After the exposure period the tubes should be enclosed in the plastic vile provided and returned to the laboratory for analysis. If not returning immediately to the lab they should be stored in the refrigerator. A 'travel blank' should also be included with each monitoring period; this tube should be taken out in the field when putting the tubes out for exposure but then stored in the refrigerator until the tubes are collected back in. It should then be returned to the lab with the exposed tubes. This 'travel blank' should highlight any contamination that may have occurred to the tubes during transit or storage. When going out in the field it is always useful to carry spare equipment with you such as clips, cable ties etc. for site maintenance.

Each batch of tubes is sent with a diffusion tube monitoring record which includes; tube no., location, tube placement (start and finish), exposure time (hours) and other data. The other data column is used to record irregularities at the site such as if the tubes were found on the ground or if they were particularly dusty etc. Irregularities such as these may affect or nullify the results and therefore it is important that they are recorded. The exposure hours must be filled in (a charge is incurred if the lab have to do this). A spreadsheet has been produced to assist in this: **SO₂ DT EXPOSURE TIMES & RESULTS JULY 1996 ONWARDS.xls** in the SO₂ tubes folder in the environmental folder.

Spreadsheet: SO₂ DT EXPOSURE TIMES & RESULTS JULY 1996 ONWARDS.xls

This spreadsheet (Figure 2) has been produced to help and record exposure information and results in one place. Before entering in data you need to copy and paste from the previous monitoring period. This will ensure that the same formulas are used.

Period	Dates	DT coordinates	Height (m)	Diffusion Tube Number	Description	Time Out	Time In	Exposure (hours)	Comments	Result (ppb)	Average of three tubes	Standard Deviation	CV
193	20/04/2011	18/05/2011			Gages High Point						#DIV/0!	### #####	#DIV/0!
194	21/04/2011	20/05/2011			Gages High Point						#DIV/0!	### #####	#DIV/0!
195					AUC Amersham						#DIV/0!	### #####	#DIV/0!
196					AUC Amersham						#DIV/0!	### #####	#DIV/0!
197					Kinsale School						#DIV/0!	### #####	#DIV/0!
198					Kinsale School						#DIV/0!	### #####	#DIV/0!
199	28 days	672		SA12S1	Plymouth PHQ	14:15:00	16:00:00	674			#DIV/0!	### #####	#DIV/0!
200	29 days	696		SA12S2	Plymouth PHQ	14:15:00	16:00:00	674			#DIV/0!	### #####	#DIV/0!
201				SA12S3	Plymouth PHQ	14:15:00	16:00:00	674			#DIV/0!	### #####	#DIV/0!
202					Top Of Jubilee Town						#DIV/0!	### #####	#DIV/0!
203					Top Of Jubilee Town						#DIV/0!	### #####	#DIV/0!
204					Lower Amersham EDM Site						#DIV/0!	### #####	#DIV/0!
205					Lower Amersham EDM Site						#DIV/0!	### #####	#DIV/0!
206					Top of Gages Road						#DIV/0!	### #####	#DIV/0!
207					Top of Gages Road						#DIV/0!	### #####	#DIV/0!
208				SA12S10	Weekes (das)	12:00:00	12:30:00	697			#DIV/0!	### #####	#DIV/0!
209				SB10S1	Weekes (das)	12:00:00	12:30:00	697			#DIV/0!	### #####	#DIV/0!
210				SB10S2	Weekes (das)	12:00:00	12:30:00	697			#DIV/0!	### #####	#DIV/0!
211					Observatory Old Towne						#DIV/0!	### #####	#DIV/0!
212					Observatory Old Towne						#DIV/0!	### #####	#DIV/0!

Figure 2 Screen print of SO₂ DT exposure times and results July 1996 onwards.xls

Columns A - C	Provide information on the dates of the monitoring period and also the number of total hours in that period. Ideally all diffusion tubes should be placed out and collected on the same day. If this is not done then as in the above example different exposure periods need to be entered and the tubes that refer to each period need to be identified. To calculate the number of hours, only enter the number of days in column A then column C will automatically update.
Column D - F	Contains info on the position and details of the site. This only needs to be updated if the tubes position changes.
Column G	This is the Tube No. This appears on the diffusion tube monitoring record – need to be updated for each period.
Column H	Provides information on the location – this should not need to be changed. Each location appears three times to correspond to the three tubes that are at each site.
Column I - J	Column I should automatically update and refer back to the previous periods column J. Update column J with the times the tubes were collected in. Provides information on the time out and time in. Column K refers to the exposure hours. When you copy and paste the previous monitoring period you will need to update the first part of the formula used in column K to correspond to the correct hours from column C.

	You will also need to make sure that the coloured names correspond to the correct colour beginning and end date.
Column L	Here should be recorded any comments that are out in the other data section on the diffusion tube monitoring record sheet.
Column M - N	When the results file is received the concentrations should be entered in here. Column M refers to the ppb concentration and Column N to $\mu\text{g}/\text{m}^3$, both of which appear on the results sheet.
Column P - T	These columns will update automatically. P – provides average of all three tubes in ppb and $\mu\text{g}/\text{m}^3$ Q – R – provides the standard deviation of both the ppb and $\mu\text{g}/\text{m}^3$ (used in CV calculation) S – T – Correlation variance calculation (explanation further on).

Once the spreadsheet has been filled in the exposure hours can be entered onto the diffusion tube monitoring record. Webobs should be updated for each site with the changeover date and time be recorded and a note made of any site irregularities and a project should be created for the next changeover.

Precision and analysis of Results

Gradko Environmental will email the diffusion tube results within 10 days of receiving the tubes in the lab. Should no results come through contact Gradko at LabReports@gradkolab.com.

Diffusion tubes are considered to be an indicative method and under European guidelines their uncertainty is defined as <20% (Environmental Scientifics Group). To improve the accuracy and precision of the diffusion tubes a co-location study can be used to calculate a bias-adjustment factor which can then be applied to the diffusion tube results (three diffusion tubes are located close to an automatic continuous analyser).

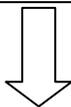
There is currently no automatic analyser that continuously measures SO_2 concentrations in use by the MVO. The Local Air Quality Management Technical Guidance 2009 (LAQM.TG(09)) (Defra 2009) recommends that triplicate exposure is used when “a more precise measurement is required, but operational or other factors rule out the use of an automatic analyser”. Since 2010 this triplicate exposure method has been adopted at MVO.

According to LAQM.TG(09) “As a rough guide, the coefficient of variation (CV) of diffusion tube triplicates is considered satisfactory when the CV of eight or more periods out of any twelve is less than 20%, and the average CV of all twelve monitoring periods is less than 10%.” The precision of the tube is considered to be poor when the CV is more than 20%. The precision of the tubes can be checked by calculating the CV of each of the triplicate tubes.

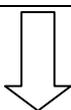
The following spreadsheet can be used to understand the precision of the tubes and also highlights outlier values and whether the precision is improved by removing these outlier values. A separate spreadsheet is required for each of the locations.

Summary Flowchart

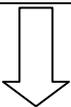
Store SO₂ diffusion tubes in a refrigerator. Tubes should be used within 12 weeks of their manufacture date.



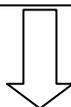
Tubes should be exposed for 4 weeks. During the changeover the travel blank should be taken out in the field with the rest of the tubes, it should then be stored in refrigerator during the exposure period. This ensures that any contamination that may occur during the time of changeover will also be picked up by the travel blank and there during the analysis the tubes can be adjusted accordingly. Make sure tubes are mounted vertically in an area of free circulation. When undertaking changeovers take spare equipment such as clips and cable ties with you for any necessary site maintenance.



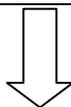
Fill in spreadsheet **SO₂ DT EXPOSURE TIMES & RESULTS JULY 1996 ONWARDS.xls** making sure to update all the relevant info/formulas. Also note if there were any factors that could influence the results such as dusty tubes or if the tubes were found on the ground etc. Then fill in Gradko Environmental diffusion tube monitoring record. Request that results files are sent in excel as well as pdf.



When results file received put results in **SO₂ DT EXPOSURE TIMES & RESULTS JULY 1996 ONWARDS.xls** and precision and accuracy file (e.g. **AEA_DifTPAB_v04_BROD.xls**). Make a note in the results spreadsheet of any outlier values that have been removed or if any values have been removed as the tubes were found on the floor etc.



Update Webobs with changeover date and time and note any site irregularities. Create a project for the next changeover date.



When reporting the values details should be given on the precision and accuracy of the results and if any values were removed due to the tubes being on the floor etc.