ESTIMATION OF ATMOSPHERIC
FLUORIDE BY LIMED FILTER PAPERS:
A REVIEW

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A research report prepared for the Atomic Energy Control Board
Ottawa, Canada

September 1988
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ABSTRACT

The limed filter paper method of static sampling of atmospheric fluoride is reviewed in this report. Use of the technique, in conjunction with precise measurement of the absorbed fluoride and calibration with dynamic air sampling techniques, to estimate atmospheric fluoride levels, is considered to give only qualitative data (± 50%). The limed filter paper method is site specific due to variations in meteorological conditions. Its main value is to indicate seasonal and annual trends in fluoride exposure of vegetation.

Subject to these considerations, the lower and upper limits of atmospheric fluoride exposure and the applicability to atmospheric fluoride estimation under routine or emergency fluoride release conditions are discussed, with special emphasis on the limiting factors.

RÉSUMÉ

Le présent rapport examine la méthode utilisant du papier-filtre à la chaux pour l'échantillonnage statique du fluorure dans l'air. On considère que cette méthode utilisée de concert avec la mesure précise du fluorure absorbé et l'étalonnage effectué grâce à des techniques d'échantillonnage dynamique de l'air ne donne que des données qualitatives fiables à environ 50 pour 100. La méthode du papier-filtre à la chaux est particulière à chaque site à cause des différentes conditions météorologiques. Sa principale valeur est d'indiquer les tendances saisonnières et annuelles de l'exposition de la végétation au fluorure.

Sous réserve de ces considérations, le rapport examine les limites inférieures et supérieures de l'exposition au fluorure dans l'air et l'applicabilité à l'estimation du fluorure dans l'air dans des conditions normales et d'urgence de rejet de fluorure, tout en insistant spécialement sur les facteurs de limitation.

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SUMMARY

The limed filter paper ("lime candle") method of sampling atmospheric fluoride has been reviewed in depth. Emphasis has been on an update since 1981, but earlier papers have been included where they are essential to the study.

The method involves static sampling of fluoride in air by conversion of CaO to CaF$_2$ and, by analogy with fluoride uptake by vegetation, is mainly intended to indicate seasonal trends in average amount and distribution of fluoride exposure to vegetation.

The method has been correlated with atmospheric gaseous fluoride (usually HF) by calibration with various dynamic sampling methods. The deposition rate is a function of the square root of the air velocity at the surface of the paper and is therefore dependent on the type of sampling station shelter and the size and shape of the paper. For these reasons, none of the published correlations are strictly comparable to each other, or applicable to the data obtained at Eldorado Resources Ltd., Port Hope, Ont, where the shelter design is apparently unique.

Nevertheless, with appropriate caution, atmospheric gaseous HF may be estimated under routine conditions using a value of deposition velocity, $V = 11$ mm/s (0.011 m/s) to convert deposition rate (ug/m$^2$/s) to gaseous concentration (ug/m$^3$) with $\pm$ 50% accuracy. 24 hour sampling times are recommended. Prolonged sampling times lead to calculation of artificially low values of atmospheric fluoride, if the level of HF is only elevated for part of the sampling period. This is because the calculation assumes a constant HF concentration throughout the period, and therefore only gives the average value, not the peak value. A sensitivity of 0.5 ug/m$^3$ is involved for a 24 hr. sampling time.
Under conditions of a large accidental release, only downwind sampling stations are of any significance in estimating exposures. If wind velocity and direction are known and they were constant, calibration of the shelter's attenuation effect will give the air velocity at the limed paper's surface and allow the applicable value of V to be obtained from the data of Wilson et al\(^{32}\), figure 1 of this report. In this way ± 20% accuracy might be achieved in calculating exposure dose, which is obtained directly. Peak exposure level may be obtained by assuming a temporal profile. Based on the experience at Sequoyah in 1986, an area several km downwind might experience an atmospheric HF concentration of several mg/m\(^3\) for 5 to 10 minutes - well within occupational limits.

An unsheltered lime paper will tolerate an exposure to 333 (mg/m\(^3\)-min) before the onset of saturation starts to reduce the value of V. In a shelter the saturation threshold will be 2 or 3 times higher.

It is suggested that the technique of preparation of limed papers be improved and that unusual emissions be accompanied by a prompt area survey with a mobile unit which uses a fast response method of analysing for gaseous HF directly. One approach which should be explored is the use of an inexpensive communications type diode laser and a multireflection optical absorption cell to measure the optical absorption of HF at a wavelength of 1.33 um.
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ESTIMATION OF ATMOSPHERIC FLUORIDE BY LIMED FILTER PAPERS - A REVIEW.

1. Introduction.

This report is intended to provide an update of the literature on the limed filter paper method of sampling atmospheric fluoride. Specific goals are: 1/ evaluate the factor for conversion from fluoridation index to atmospheric fluoride concentration 2/ evaluate the limed filter paper method in terms of calibration methods, accuracy, sensitivity, upper limit and limiting factors 3/ evaluate the applicability to monitoring a hypothetical large accidental fluoride release at a UF₆ facility, as well as its use under routine conditions 4/ discuss the fluoride monitoring methods, and their relative merits, used at UF₆ facilities or other industries in other countries.

There are various industrial sources of fluoride emissions to the atmosphere¹-⁵, notably aluminium smelters, the steel industry, phosphate fertilizer plants, production of ceramics and bricks, and combustion of coal. These may result in atmospheric fluoride levels of from 1 to 10 ug/m³ in neighbouring areas¹. An accidental release of HF from a chemical plant can result in more than 50 ug/m³ for a few hours¹. UF₆ production plants have the potential for atmospheric fluoride releases, but have historically been relatively minor sources³,⁶ compared to the above. Worldwide, volcanoes are the greatest source, releasing up to 7 x 10⁶ Mg of fluoride per year into the atmosphere². Table 1 summarizes the most common sources of atmospheric fluoride.

Atmospheric fluoride (mainly HF) may be readily absorbed by plants, as may fluoride in water soluble particulate form (eg
NaF). Some plants suffer damage at atmospheric levels as low as 0.5 ug/m³ 5,7-9. Herbiverous animals can accumulate fluoride via their food chain - some types are less sensitive to fluoride than others. Humans can tolerate quite high atmospheric fluoride levels before experiencing temporary eye or breathing discomfort. The occupational exposure threshold limit value (TLV) was 2.5 mg/m³ for a 40 hr. work week13 in Kentucky in 1984.

There have been a number of recent reviews of biological and environmental effects of atmospheric fluoride1-5,7-12. These are mentioned for completeness as these effects are not the subject of this report.

The process of converting UO₃ to UF₆ involves the use of HF and F₂. As in any chemical plant, equipment maintenance, malfunction, failure, or operator error will lead to low level releases to the atmosphere6,14. F₂ reacts with moisture to form HF, O₂ and some O₃, though below a few ppm it may persist for 20 to 30 min⁴. There is also the possibility of a major incident giving a large short term release (see Section 7). UF₆ itself forms HF and particulate UO₂F₂ on interaction with moisture in the atmosphere¹⁵, so the potential for UF₆ release is also of concern.

In Canada over the past several decades, there have been major investigations of four separate industrial sources of fluoride releases. These were at:

-Port Maitland, Ont. (Hall Commission, 1968¹⁶).
-Kittimat, B.C. 1975-78¹⁹.
-St. Regis, Cornwall Island, Ont., 1965-1975⁷,²⁰.

The first two cases involved nearby phosphate fertilizer and elemental phosphorus production, while the latter two involved
aluminium refineries. These cases were reviewed in a 1984 Quebec government report\textsuperscript{20} to lay the foundation for an evaluation of numerous industrial fluoride sources in Quebec. The two Ontario cases were reviewed by Linzon\textsuperscript{7} in 1978.

Cornwall Island atmospheric fluoride levels continue to be monitored by the federal Environmental Protection Service\textsuperscript{21}. Ontario and federal fluoride regulations and objectives are given in tables 2 and 3.

At Port Hope, Ont., Eldorado Resources Ltd. converts UO\textsubscript{3} to UF\textsubscript{6} for export sale to 235U enrichment facilities. For many years the Ontario Ministry of the Environment (OME) has monitored fluoride deposition on limed paper (which they refer to as the "fluoridation index" see Section 2) in the surrounding area, with observations generally well within the limits given in table 2. Eldorado has also had its own monitoring program based on the limed filter paper method. R.E. Lamarche reviewed some aspects of the method and of Eldorado's results, in a 1982 report\textsuperscript{22}. Eldorado's fluoride release goals (100 g/hr) and OME data from 1969 to 1981 are presented in a 1984 federal Environmental Protection Service report\textsuperscript{23}.

Since 1982, Eldorado has expanded its monitoring program. In addition to nine 30 day limed filter samples, they routinely do six 24 hr. and five 7 day exposures at various locations at the property boundary and in neighbouring areas of Port Hope. From 1982 to 1985, Eldorado operated a continuous monitor (Phillips, air bubbler plus fluoride specific electrode potentiometric analysis (see Section 3)). This was expensive and was discontinued because fluoride levels were always below OME limits. Eldorado also currently operates a continuous stack gas monitor (Braun-Lube, air bubbler plus fluoride specific electrode) which of course gives much higher fluoride levels than are found at ground level, at a distance\textsuperscript{12}. 
2. The Limed Filter Paper Method: General Description.

There are a number of variations of the technique, with different support materials (filter paper, fibre glass), different "fixant" (calcium oxide, calcium formate, sodium hydroxide, sodium formate, potassium carbonate), different sizes (0.6 to 9 dm$^2$), different shapes and orientations (flat, cylinder, both sides, one side, vertical, horizontal), different shelters (none, v-roof with open side, louvred sides, solid side - open soffit - open bottom, inverted Petri dish and others), different exposure times (commonly 1 to 4 weeks) and different recipes for coating or impregnating a plate or filter paper.

The original concept was to impregnate a filter paper with CaO by dipping it in a slurry of Ca(OH)$_2$ and drying it. The coated filter paper is then exposed to the atmosphere, usually in a small shelter several feet above the ground. Fluoride in the atmosphere, principally gaseous HF, reacts with the CaO to form CaF$_2$. In the laboratory, the CaF$_2$ is dissolved, the pH and ionic strength of the solution adjusted and buffered to match that of a standard, and the fluoride measured potentiometrically with a fluoride specific electrode (FSE).

Depending on the industrial source, atmospheric fluoride may be gaseous molecules (HF, H$_2$SiF$_6$, SiF$_4$, BF$_3$), gas molecules adsorbed on particulate matter, and particles such as UO$_2$F$_2$, cryolite (Na$_3$AlF$_6$), AlF$_3$, CaF$_2$, FeF$_3$, NaF, Na$_2$SiF$_6$, PbF$_2$. The limed filter paper method, particularly when the paper is suspended vertically, is insensitive to particulate matter.

The concept was never intended to measure atmospheric fluoride. It was developed to give an estimate of the rate of deposition of fluoride from the atmosphere on to the surface of vegetation and to determine relative seasonal trends. Current practice is to refer to "deposition velocity" $V$, which is the ratio of the deposition rate (D.R.) (fluoridation index) converted to m$^2$
area and exposure time in seconds, $\text{ug/m}^2/\text{s}$, to the atmospheric HF concentration $\text{HF}_g$ (ug/m$^3$), and has units of ms$^{-1}$ or $10^{-3}$ mm s$^{-1}$ (eg. $0.011$ m/s = 11 mm/s) (see equation 1)$^{24,34}$. At $25^\circ$C, 1 ug HF/m$^3$ corresponds to 1.2 ppb in air.

$$\text{D.R.} (\text{ug/m}^2/\text{s}) = V(10^{-3}\text{mm/s}) \times \text{HF}_g(\text{ug/m}^3) \quad \ldots(1)$$

A bewildering range of units appears in much of the literature; use of $\text{ug/dm}^2$/day, week or month is common. Units of $V$ in the past have been as diverse as $\text{m}^{-3}/\text{dm}^2$/day$^{27}$ to $\text{ug/dm}^2$/ppm-min$^{32}$ and it is not uncommon to find a modern review with incorrect values of $V$ due to errors in conversion from the units of the original publication. Table 4 gives various conversion factors between units and a typical calculation.

The key feature of the limed filter paper method is that it is a static sampling method, to simulate the interaction of vegetation with the atmosphere. This feature leads to a major characteristic of the method, the dependance on air velocity, discussed in Section 4.


In order to show a correlation between fluoride deposition rates and atmospheric emissions from an industry, or effects on local vegetation, it has been necessary for researchers to measure fluoride levels in the atmosphere and in the vegetation for the same location and time period as the limed filter paper exposures. The atmospheric measurements all involve dynamic sampling. Air is aspirated through the sampling device at a metered rate. There may be one filter paper, impregnated with NaOH, which captures particulates and reacts with HF to form $\text{NaF}^{24}$. However to separate gas from particulates this must be preceded by another filter paper, commonly impregnated in citric acid, which transmits HF to the second filter but catches particulate matter$^{18}$. Sometimes a citric acid treated filter paper, followed by an
impinger is used—a metered amount of air is bubbled through an alkaline solution. Dual tapes are often used, analogous to the dual filters mentioned above. Another approach is to use a bicarbonate coated glass tube, followed by a particulate filter.

The analytical standards literature does not list the single filter (alkali impregnated) collection method except for use as a personal dosimeter (see section 9). For measurement of atmospheric fluoride concentration in the area surrounding an industry, it is preferable to be able to measure both the gaseous and particulate components.

The dual tape collection method is ASTM standard method D3266-79. It has the advantage of providing a breakdown in time for fluoride deposition data, as the tapes are advanced a certain amount at programmed time intervals, and the exposed portions are stored on a reel. The ASTM procedure indicates ±16% standard deviation for 1 to 3 ug/m^3 and ±5% for 12 to 45 ug/m^3. Milne was able to measure HF backgrounds of 0.05 to 0.15 ug/m^3 with an accuracy of ±0.14 ug/m^3 but he had to significantly modify a commercial apparatus to achieve this.

The dual filter method is analogous to ASTM method D3266-79 but gives data for only one sampling period. This can be short if the rate of air aspiration is high. The method is recommended by the Standards Association of Australia, the U.K. Health and Safety Executive, and the Ontario Ministry of the Environment. The Australians claim ±10% for 24 hr sampling (50L/min) of air containing 0.1 to 10 ug/m^3 of HF. The U.K. procedure must be for personal monitoring because they give a detection limit of 100 ug/m^3 in a 20L air sample and ±10% for 120 L samples at 50 ug/m^3 to 10 mg/m^3. The Ontario Ministry of the Environment claims a limit of detection of 0.2 ug/m^3 for a 24 hr, 15L/min sample. They use a commercial instrument, Metrex SAS-4, developed by the Ontario Research Foundation years ago. MOE also cite the ASTM - D3266-79 precision data. Environment
Canada uses this method for its monitoring program at Cornwall Island. 

For calibration of the response of lime - or other alkali - treated papers (see Table 7), the dual tape method was used in references 28 and 30 and the dual filter method was used in reference 18.

Another fairly common collection method is ASTM D3268-85, which involves a sodium bicarbonate - coated glass tube followed by a particulate filter. This applies to 12 hr sampling periods, collecting 2 to 500 ug HF at 14.2L of air/min, or about 0.2 to 50 ug/m$^3$. For sampling periods of 15 to 120 min., HF collection is better than 95% up to 40 ug. From 0.5 to 3.3 ug F/m$^3$, the RMS difference of duplicate coated tubes is 0.05 ug/m$^3$. Some particles tend to stick to the walls of the tube, rendering particle collection and analysis less satisfactory. Israel used this method, as well as the dual tape method, to calibrate atmospheric concentration for his limed paper work. The main possible advantage is that by eluting the fluoride from the tube wall with a small volume of water, high sensitivity may be achieved. However Milne believes that the method requires too much skill and the tubes are too fragile for use outside the laboratory.

The filter and impinger (bubbler) method - ASTM D3267-80 is also encountered in the literature. A commercial model, the Kyoto HF 18 was evaluated by Milne. With significant modification and calibration he felt that the method is potentially the most accurate, limited mainly by the accuracy of setting up calibration gases with cumulative errors amounting to about 0.15 ug/m$^3$ at the 1 ug/m$^3$ level. However this method is less rugged than the dual tape samplers and apparently requires a mobile caravan type monitoring station. Milne's data on precision are similar to those given by ASTM. The method gives a continuous reading. It was used by Eldorado for a time, using a Phillips apparatus, as mentioned earlier. Lynch et al used the method
for air measurements in conjunction with their measurements of fluoride deposition on CaO plates.

The above collection methods are all followed by FSE analysis, described in ASTM method D3269-79, section 11. The recommended range is 0.1 to 10 ug F/ml of solution. Below 0.1 ug/ml there is a slow response time and non linearity. This gives a lower limit of detection of 1 ug/m³ for fluoride in the atmosphere if the air sample volume is 10 m³ and the total sample is collected in 50 ml of solution. The solution potential in mV is compared to a calibration curve for standard solutions at the same pH and ionic strength. The latter are based on a weight of NaF. The relative standard deviation is 2.9 to 5.8% and relative errors are 0.2 to 4.9%. In wind tunnel experiments with very high HF levels, filter papers were analyzed by a colorimetric titration, while the air concentration was measured by conductimetric measurements on the solution obtained from a capillary type air/liquid scrubber. The colourimetric titration is one of the accepted methods described in ASTM method D3269-79.

The various methods of atmospheric fluoride sample collection and analysis are summarized in table 5.

4. Conversion Factor Between Fluoride Deposition Rate and Atmospheric Fluoride Concentration; Main Factors Which Affect Its Value.

It is desired to estimate the best value of the conversion factor V for use in converting Eldorado Resources Ltd's filter paper fluoride deposition data (as ug/m²/s) to atmospheric HF concentration (ug/m³). To do this we must highlight the main factors which influence the value of V, define these factors as they pertain to the Port Hope monitoring stations, and then identify the most comparable data of adequate quality in the literature. The divergence of published methods renders any statistical approach (correlation factor) impossible.
The most dominant factor is the air velocity on which $V$ shows a strong dependence. The limed paper literature refers to an aerodynamic resistance. Chemical engineers would refer to a gas-solid diffusion barrier to mass transfer in a thin layer above the CaO. The concept is well documented in the personal dosemeter literature.

In a model of a directly analogous situation, atmospheric SO$_2$ deposition on a PbO$_2$ plate, Liang et al have demonstrated that where the solid phase reaction is fast and the gas phase resistance is rate controlling, the deposition rate is independent of absorber concentration and is dependent on the gas phase pollutant concentration and on the square root of the air velocity at the surface.

Wilson et al., in highly controlled and characterized wind tunnel experiments, exposed vertically suspended 0.7 dm$^2$ limed filter paper cylinders (unsheltered) to measured high levels of HF in air (1 to 63 ppm, 833 to 52,500 ug/m$^3$) for measured times. They found that the deposition velocity $V$, expressed in units of ug/dm$^2$/ppm-min., was independent of HF concentration, meaning that deposition rate depends linearly on gas phase HF concentration. A replot (see table 6 and figure 1) of the average values of their data for $V$ (excluding those obtained above 400 ppm-min, which involve partial saturation), against the square root of the air velocity, is a reasonable straight line through the origin especially if we reject the value at 18 mph (2.23 m$^{1/2}$/s$^{1/2}$). The authors' original units of ug/dm$^2$/ppm-min and mph have been converted to deposition velocity and air velocity in metric units. Similarly, the wind tunnel data of Mukai and Ishida have been converted (table 6) and replotted (figure 1). Again there is a reasonable square root dependence on air velocity. The deposition velocities are about 50% higher because they used a 5cm flat paper, which offers less aerodynamic resistance than the cylinder used by Wilson et al. It is concluded from these results that the limed filter paper method involves predominant control of the fluoride deposition rate via the gas phase resistance.
Davison and Blakemore\textsuperscript{28} compare the calculated aerodynamic resistance to the total resistance for the wind tunnel experiments of Wilson et al.\textsuperscript{32} and Mukai and Ishida.\textsuperscript{31} The total resistance is just the reciprocal of the deposition velocity. They conclude that the surface resistance is significant, especially in the former case. However the calculation is not explained. A factor of only 2 increase in the calculated value of $r_a$ would result in agreement with the conclusion that the gas phase resistance is rate controlling.

Thus it is air velocity at the filter paper surface which is important. For this reason, the design of the shelter and the geometry (including size) of the limed filter paper will play a major role. The shelter effect has been understood qualitatively for a long time. For example Wilson et al.\textsuperscript{32} showed that $V$ could be reduced to 40\% of its unsheltered value by some shelter designs, in their wind tunnel experiments. Davison and Blakemore\textsuperscript{28} noted that external air velocity is reduced by a factor of 10 at the paper surface inside a double-louvred Stevenson screen, which would reduce $V$ by a factor of 3.2. Apart from reference 28, the geometry effect is not mentioned in the literature on fluoride deposition measurements, though it is well known in the field of gas-liquid or gas-solid mass transfer, for example in catalysis studies.

The predominantly gas phase mass transfer resistance is the reason why there is little effect of using a fixant other than CaO to chemisorb fluoride (e.g. Ca formate, NaOH, Na formate), since solid phase reaction rate is not controlling. There is an exposure saturation factor for CaO, but it appears to arise at doses greatly exceeding those encountered in the Eldorado work.\textsuperscript{22,23} Wilson et al. found $V$ to fall off above filter paper depositions of 7000 to 8000 ug F/dm$^2$ (exposure to "400 ppm-min")\textsuperscript{32}. Their limed filter papers contained about 80mg CaO/dm$^2$ with a theoretical maximum fluoride chemisorption of 50,000 ug F. The effect presumably arises from the creation of a second mass transfer barrier, this time solid phase CaF$_2$, through which HF
must diffuse before encountering and reacting with CaO. In the extreme limit of solid phase resistance (surface resistance in terms of reference 28) control, the deposition rate would depend on the square root of the gas phase fluoride concentration and be independent of air velocity45.

Outdoors, another saturation effect has been noted by de Temmerman et al24 after several weeks exposure at several ug/m³ HF in the atmosphere. They conclude that in the case of a 28 day exposure, the fourth week results in negligible fluoride deposition on the limed paper. They state, without supporting evidence, that atmospheric CO₂ has reacted to convert CaO to CaCO₃ which reacts with HF more slowly. They see the effect at less than 10% of the total deposition level, indicated by Wilson et al as the threshold for CaO saturation. Their interpretation is not consistent with the conclusion above, that gas phase mass transfer resistance predominates, and they do not provide supporting evidence.

Wind direction and precipitation are of obvious importance to outdoor monitoring situations. Various publications in which V is measured, deal with the effect of these variables by using seasonal averages of the data. They often do not measure wind velocity.

As for calibration, the colorimetric titration and FSE analyses are easily calibrated by weighing microquantities of titrant or of NaF to prepare a standard solution. However calibration of the sampling efficiency of the various devices used to measure the gas phase HF concentration is handicapped by the difficulty of accurately simulating mixtures of a few ppb of HF in air, due to the reactivity of HF with various surfaces36. Wilson et al32 worked at up to 63 ppm of HF, making the gas phase analysis fairly easy. However the values of V obtained by Bourbon and Riouful in 198425 and by de Temmerman and Baeten in 198624 are further discounted for our purpose because their gas phase calibration involved the single filter, dynamic sampling method, which
combines the gaseous and particulate concentrations. We wish to relate to gaseous HF only.

Table 7 gives a summary of data on V, published since 1967. With the exception of Wilson et al.32, and Mukai and Ishida31 (no shelter), they all involve shelters of different design from that at Eldorado and usually from each other. The measurements of Lynch et al.29 and Sidhu18, two Environment Canada projects, involve partial shelter by the wall of an inverted petri dish.

Eldorado Resources prepares a 1 dm$^2$ (100 cm$^2$) rectangle of filter paper by dipping it in an aqueous slurry of 100g Ca(OH)$_2$/litre. About 500 mg of CaO is on the filter paper - much of it is visible as a superficial coating on top of the paper. The slurry is a factor of 5 higher in Ca(OH)$_2$ content than for any case in table 7, and a factor of 10 above the level recommended to prevent CaO from flaking off. The OME filter papers are impregnated in a 2% lime slurry. The amount of CaO on Eldorado's papers may be irreproducible; 500mg CaO/dm$^2$ is a factor of 10 higher than in the work of Wilson et al.32 where the limed paper was able to tolerate high exposures before saturation set in (7000 ugF/dm$^2$), equivalent to an exposure to atmospheric HF at a level of 24.5 ug/m$^3$ for 30 days with a deposition velocity $V = 11$ mm s$^{-1}$. Note that limed papers with 30 day exposure give much lower deposition rates than the sum of 4 one week exposures at Eldorado Resources. This effect may be due to flaking or erosion of the excess CaO, with the wind carrying this material away. The saturation effect discussed above would result in a tendency towards a plateau value of fluoride deposition versus time, not a reduction at long exposure times.

The Eldorado Resources limed papers are wrapped around a cylindrical form about 4 inches high and placed vertically inside a shelter comprised of a stack of inverted cones, spaced to give a louvre effect. The size and geometry of the limed paper is
about the same as in the work of Wilson et al\textsuperscript{32}. The latter used no shelter but all the other data in table 3 have even less in common since they involved both different geometry and different shelter design.

Table 8 summarizes the many variations in the technique.

It is concluded that there is no direct comparison between the limed filter paper technique at Eldorado, and any of the calibration experiments reported since 1967 (table 3). However there is identical filter paper geometry to that in the work of Wilson et al. The latter is also a reasonably quantitative work—controlled experiments in a wind tunnel with accurately measured HF levels from 833 to 52,500 ug/m\textsuperscript{3}. These levels are also relevant to considerations of direct high level exposure to humans, over a short period (see Section 7), whereas the other reports deal with long term low level exposures. The wind tunnel data of Mukai and Ishida\textsuperscript{31}, covering a range of 41 to 174 ug/m\textsuperscript{3} involve a different (flat) paper geometry.

Values of $V$ in table 6 are much higher than the other values in table 7, which average $11 \pm 3$ mm/s if we exclude the low value of Sidhu. The latter reflect the attenuation of air velocity by a shelter, and the associated reduction in the observed value of $V$. From the plot of the data of Wilson et al\textsuperscript{32} in table 6, figure 1, one can deduce that the air velocity at the surface of the papers, inside a shelter, was around 0.71 m/s or 1.6 mph on average, for $V = 11$ mm/s and cylindrical filter papers.

One may conclude that the use of the value $V = 11 \pm 3$ mm/s is as good as any approximation to evaluate the seasonal, site averaged air concentration of HF (with a probable accuracy of $\pm 50\%$) from seasonal site averaged limed filter paper deposition rates. This value is some sort of average over various geometries, shelter designs, wind velocities and exposure times.

However for more precise short term work for accident evaluation,
it is better to work from the unsheltered values of Wilson et al\textsuperscript{32}, namely 21.5 and 43 mm/s at air velocities of 1 and 4 m/s. One can measure values of wind velocity at the sample station, and calibrate the effect of the shelter on the air velocity at the limed paper surface, should the need arise. If the latter is 40\% of the external air velocity, then $V$ will be 13 and 28 mm/s respectively, for air velocities of 1 and 4 m/s outside the shelter. Again these numbers relate to a cylinder of external area approximately 1 dm\textsuperscript{2}.

5. **Levels of Atmospheric HF Which May be Estimated With Limed Paper.**

The applicability of limed filter papers to measurement of atmospheric HF has been partly discussed above and more discussion will follow. Subject to these considerations, one can evaluate the range of HF concentration which may be semiquantitatively estimated.

The lower limit may be derived from the sensitivity of the FSE method, which corresponds to 5ug for a 1 dm\textsuperscript{2} limed paper at Eldorado's laboratory. The analytical sensitivity, at the Paducah Gaseous Diffusion Plant, is the same – 5ug HF per sample\textsuperscript{13}. However dynamic air sampling at Paducah means that the limit of detection is 0.1 ppb or 0.08 ug/m\textsuperscript{3}. The static sampling approach at Eldorado results in a limit of detection equal to 0.5 ug/m\textsuperscript{3} for 24 hr. exposures, and proportionately lower for longer exposures.

For short exposure times, the upper limit is given by the data of Wilson et al\textsuperscript{32}. The deposition velocity falls off above a fluoride deposition of 7000 - 8000 ug/dm\textsuperscript{2} or an exposure of 400 ppm-min in that work where $V$ was about 3 times higher (equivalent to an exposure to 33.3 mg/m\textsuperscript{3} for 10 min. with $V$=34 mm/s) than it is on average in sheltered sampling stations. For accident analysis, it is this high level, short exposure type of situation which is relevant.
For a special application such as analysis of possible fluoride exposure associated with an accidental release, the value of \( V \) may be estimated as discussed in the last paragraph of Section 4. The threshold for the onset of saturation for a sheltered limed paper with \( V=11 \, \text{mm/s} \), will be about 1200 ppm-min or 1000 mg/m\(^3\) - min. This gives an upper limit of gaseous HF exposure which may be measured, eg 33.3 mg/m\(^3\) for 30 min (with \( V = 11 \, \text{mm/s} \), ie a sheltered limed paper). The limit may be increased by calibration of the saturation effect.


Under routine circumstances, the problem of fluoride loss from 30 day exposure papers is the worst limitation. This could arise from loss of CaO. Short exposure papers don't suffer this problem, though with high CaO loading used at Eldorado, 24 hr. exposures also give somewhat low fluoride levels\(^22\).

The next most troublesome factor is the lack of knowledge of air velocity at the surface of the filter paper, or even the velocity outside the shelter. A variation of a factor of 3 in the value of \( V \) can be involved at different sample stations at the same time, or at the same station at different times. This can arise from variations in wind speed and direction, as well as possible perturbations by buildings. The latter can give high numbers due to a corridor or channelling effect, then rapid dilution by enhanced dispersion in the wake of a building\(^6\).

Precipitation during the sample period will of course result in an apparently low fluoride exposure to the limed paper even if an unusual fluoride emission level existed for some of the time.

The fluoride deposit on the limed paper reflects the integral of the atmospheric HF concentration over the length of exposure. Suppose that a 7 day exposure involved 24 hrs. at 10 ug/m\(^3\) and the rest at 0.5 ug/m\(^3\). Assuming a deposition velocity
V = 11 mm/s one will observe a deposition of 123.5 ug/dm$^2$ with 95 ug/dm$^2$ arising from the 24 hour excursion. However the analyst will average the fluoride deposition over the 7 days and conclude that the average atmospheric fluoride level over the 7 days was 2.2 ug/m$^3$. The problem doesn't arise if one is monitoring the integrated exposure to vegetation (see table 2, Ontario fluoridation index regulatory limits), but the numbers will mislead one who is attempting to assess occasional excursions in atmospheric fluoride concentration. Today of course, Eldorado's stack gas monitor makes up for this to some extent, though one could not expect any correlation with other than a down wind ground station for a given excursion. Neither does this information relate to ground level emissions.

These points may be illustrated from actual operational data. In the Oct. 1987 Port Hope environmental compliance report to the AECB, the weekly average stack gas fluoride emission for week 43 was 827 g/h and the month average was 559 g/h, compared to a one week action level of 330 g/h. The site-averaged 30 day lime paper deposition was 95 ug/dm$^2$/30 days for October 1987. If the applicable value of the deposition velocity was V = 11 mm/s, we deduce that the month's ground level atmospheric fluoride, averaged over all the sampling stations, was only 0.33 ug/m$^3$. One expects the value to be reduced by the beneficial effect of stack height, but the value in week 43 could well have been 1.3 ug/m$^3$, artificially averaged to 0.33 by the 4 week exposure time. Indeed, sample station 6 gave 90 ug/dm$^2$/7days in the week of Oct 21-28. At the same location, the Oct 23-26 weekend sample gave 40 ug/dm$^2$/day. For V = 11 mm/s these numbers correspond to 1.35 ug/m$^3$ for Oct 21-28, and 4.2 ug/m$^3$ for the weekend of Oct 23-26. These data show the averaging effect of prolonged sampling times and it is quite possible the fluoride level was higher than 4.2 ug/m$^3$ for part of the time at station 6. The stack emission levels on that weekend were 591, 877.6, 540.4 and 1906 g F/h, Oct 23 to Oct 26.

The fact that only the downwind sample station is of any value is
also confirmed. During October 1987 the predominant winds were from the northwest (29%) and from the west (17%). Only station 6 detected any fluoride during week 43. It is on the east wall of the harbour just outside plant property and about 150 metres east of the east plant. Figure 2 illustrates the above information on a map of Port Hope.

Another deficiency of the limed filter paper method is its inability to measure particulate fluoride\(^{30}\). However Eldorado carries out separate dust fall measurements. The main particulate of interest is HF adsorbed on dust particles, since that may be dissolved by moisture on the surface of a leaf. Water soluble NaF particles are of concern for possible harm to vegetation near other types of industry, but should not be a concern at Port Hope. UO\(_2\)F\(_2\) aerosol particles, formed by hydrolysis of any escaped UF\(_6\) only represent a hazard to vegetation if they are water soluble - UO\(_2\)F\(_2\) does form a crystalline hydrate\(^{15}\). UO\(_2\)F\(_2\) is much less toxic to humans than HF\(^{46}\).

For completeness, one should mention that vegetation can compete with a limed filter paper for fluoride deposition\(^{47}\). This can in principle cause an erroneous low result, though this point is probably only relevant to monitoring stations outside Eldorado's property.

The factors which limit the use of limed papers in measurement of atmospheric fluoride, are highlighted in table 9.


The discussion in this section relates to the possibility of using limed paper fluoride deposition to estimate the fluoride exposure to humans in the area. It is perhaps useful to first establish an atmospheric fluoride level which might be encountered.
There are several estimates in the literature for accidental UF₆ releases. In the 1974 USAEC report WASH 1248¹⁴ an accident is hypothesized in which a 2.5 ton UF₆ cylinder ruptures due to overpressure on heating. 700 kg. of UF₆ is released into the room in 35 minutes. This is exhausted through a scrubber system, a high efficiency particulate air (HEPA) filter and out the stack. On release the UF₆ hydrolyzes due to moisture in the air and in the scrubber system, making UO₂F₂. The UO₂F₂ aerosol¹⁵ plugs the HEPA filter, destroying the negative pressure differential and allowing UF₆, UO₂F₂ and HF to seep from the building. This results in 1% of the uranium and 10% of the HF being released from the building at ground level. At a distance of 100m, a level of 3.5 mg/m³ (4.2 ppm) of HF would arise. Conceivably someone might be exposed to this level of HF for 2 hours. In 1974 the recommended occupational TLV was 2 mg/m³ for an 8 hour day. Hence the exposure would only be 14% of the dose which in 1974 was felt would result in temporary eye or breathing discomfort. A more recent accident release analysis from Japan points up the dependance on filter performance but deals with comparable initial release figures⁴⁸.

In 1984 at the Paducah UF₆ enrichment plant in Kentucky, the occupational 40 hr TLV was 2.5 mg/m³. In 1979 the U.S. National Academy of Sciences set HF emergency exposure limits for military and space agencies as 16.7 mg/m³ (10 min), 8.3 mg/m³ (30 min) and 6.7 mg/m³ for 60 min. The levels for F₂ are 5 to 8 times lower⁴.

On Jan 4, 1986 there was an accident at the Sequoyah Fuels Corporation facilities at Gore Oklahoma⁴⁹. A 14 ton UF₆ cylinder was overpressurized due to being overfilled (29,500 lbs.). When warmed in a steam chest the 12 ft. long cylinder developed a 52 inch long split in the wall, 8 inches wide at its mid point. There was a massive release of UF₆, probably 75% in 5 min and the rest in the next 40 min. The UF₆ promptly hydrolyzed forming HF gas and an aerosol of UO₂F₂. A worker
in a scrubber building 50 ft away was promptly enveloped in the plume. He died several hours later. There was an attempt to limit the release by hosing down the area. It is estimated that this washdown carried about 50% of the fluoride into the emergency pond so the cloud would have been about 6700 kg of UF₆, forming 5900 kg of UO₂F₂ and 1500 kg of HF.

With the aid of an atmospheric transport, diffusion and deposition model, (valid for plume behaviour from 1 km. downwind) it was calculated that the peak 10 min air concentration was 1 mg/m³ in a residential area nearly 6 km away (see pages 20, 21 and 33 of reference 49).

There were some sort of air sampling stations in operation ("air drawn through filters"). The fluoride analysis of these was discounted since they were not subdivided to allow independent analysis. However the uranium analysis at these stations, multiplied by 0.26 (from the mass balance of the reaction which forms UO₂F₂ and HF), gives an estimate of HF. This procedure gives a high value at one station at about 200 m just inside the property - a 10 min average of 31 mg/m³, and a 60 min. average of 5.2 mg/m³.

Hence there exists the possibility of exposure, to 30 mg HF/m³ for 10 min and one sixth of that for an hour, 200 m. downwind. At greater distances, an exposure of 10 (mg/m³-min) seems possible at 5 or 6 km.

If the goal is to estimate the exposure to HF, of an individual who happens to encounter the downwind plume, it would be necessary to have a limed paper monitoring station somewhere along the path of the plume. We know from section 5, that an unsheltered lime paper will tolerate an exposure of 333 (mg/m³-min) before the onset of saturation starts to reduce the value of V. A sheltered station would likely tolerate triple that exposure due to the reduced air velocity inside the shelter.
To achieve the ± 20% accuracy found in the wind tunnel work, it would be necessary to know both the wind speed at the monitoring station, at the time the HF plume passes, and the shelter's attenuation effect on the air velocity at the surface of the limed paper. This information would allow one to calculate the applicable value of V. One now exploits the fact that the limed paper integrates the exposure concentration x time. In other words if one measures the deposition of fluoride as ug/m² and divides by $10^{-3}V$ where $V$ is in mm/s, one obtains the gas concentration ug/m³ x exposure time in seconds. An estimate of exposure time would allow the peak concentration to be estimated. Presumably however the product (mg/m³-min) is the important figure for purposes of estimation of exposure of humans to fluoride.

If the monitoring station is in the path of the HF plume, but not close to the person who may have contacted it, there are sophisticated plume transport and dispersion models in the U.S. which may be applied to estimate the exposure at other points along the path of the plume. The OME is developing its model to a more sophisticated level.

One set of possible circumstances would be of considerable concern to anyone who is attempting to calculate fluoride exposure of humans in an accidental release situation. A wind could blow the HF plume to a residential area and then fall to zero. The zero wind velocity would cause a very low value of deposition velocity $V$ and hence a low amount of fluoride would be deposited on a limed paper, per unit time. This observation would cause an observer to conclude a low value for atmospheric fluoride, if the peak wind velocity is used to estimate $V$. Contrary to this deduction, people in the area could be exposed to a stagnant, high level of HF, if the wind falls off.

For hazard estimation where neither wind velocity nor shelter attenuation effect are known one could use $V = 11 \text{ mm/s}$ to estimate the fluoride exposure of the limed paper with a probable ± 50% accuracy.
8. Monitoring Atmospheric Fluoride Releases at UF₆ Facilities or Other Industries.

The approach to atmospheric monitoring at Eldorado's Port Hope UF₆ production facility, was discussed in section 1. From the outset, according to OME officials, the philosophy was to relate directly to the possible hazard to vegetation by using lined filter paper as a surface deposition technique. In 1984, Environment Canada recommended that this qualitative approach be supplemented by periodic direct measurements of atmospheric fluoride, to give a basis for correlation with releases from the plant. It also suggested an on-site meteorological station (re wind speed and direction etc.) if adequate data are not available from nearby weather stations.

Little information has been found concerning fluoride monitoring at other UF₆ facilities. In the U.S.A. the policy, since the early seventies at least, has been to measure atmospheric fluoride by dynamic air sampling methods. The report WASH 1248 states that historically, less than 2 ppb (1.6 ug/m³) of fluoride in the air, on average, has been measured near "wet process" UF₆ plants. Unfortunately the report does not mention the methods of HF analysis. In 1972 the Portsmouth UF₆ diffusion plant used an impinger + FSE analysis. If there was a prefilter this would correspond to method ASTM D3267-80. The highest observed fluoride level was 5 ppb (4.1 ug/m³) and the average was 0.8 to 1 (0.8 ug/m³). At Paducah, Kentucky, the filter plus impinger method ASTM D3267-80 was used up to 1974. Since then they have used the dual filter analog of D3266-79, with FSE analysis every 7 days. Up to 1977 there were excursions up to 24.5 ugF/m³. In 1977, after the UF₆ feed plant was put on standby, and only the diffusion (enrichment) plant operated, the highest level was 1.4. Paducah had the lead role among USDOE facilities in developing sampling protocols, analytical techniques and an adequate averaging time. In 1981 there were 4 air sampling stations at the site perimeter and 5 about 1.6 km from the perimeter and others out to 8 km.
Observations were compared with calculations based on two models - "Atmospheric Transport Model" and "Climatological Dispersion Model" from ORNL and the Environmental Protection Agency respectively. They found rapid dilution by dispersion, to near background levels, within the property (350m)\(^6\).

At the Sequoyah UF\(_6\) facility, where the 1986 accident occurred, we are just told that air monitoring involved drawing air through filters, presumably the same as at Paducah\(^6\). Since that accident, there has been a study of devices which might give "automated continuous or rapid intermittent remote sensing to provide an alarm at a threshold value (absolute response) or when a significant emission excursion has occurred (rate of change of response)." Laser light scattering by UO\(_2\)F\(_2\) particles did not work very well. A "Sensidyne HF Alert Monitor" (an electrochemical sensor) worked well, but hydrated HF forms a dense mist near the ground and the monitor relies on convection to give results. The "Gastec HF Detector Tube" was sensitive but presumably only operates when triggered by some mechanism. It is a tube filled with a pH indicator which changes from yellow to pink when exposed. The migration distance for 4 syringe pump strokes, calibrated for nominal 0.5, 1, 2, 5, 10, 15 and 20 ppm (20 ppm = 16.7 mg/m\(^3\)) is marked on the tube (10 ppm corresponds to about 1.9 cm). For higher levels, fewer strokes may be used. Calibration is affected by relative humidity\(^46\).

At the British Nuclear Fuels UF\(_6\) production facility (Springfields Works, Salwick, Preston, Lancs., U.K.), HF is determined by the "Chemcassette Monitor" (MDA Scientific). The method is based on HF induced changes in optical reflectivity of a treated tape. MDA claim rapid response and 0.7 to 30 ppm (0.6 to 24.6 mg HF/m\(^3\)) detection range. This range is useful for occupational or accident exposure situations, but not for routine monitoring of ug/m\(^3\) levels of atmospheric HF. No information on this method was found in the literature.

As far as other industries are concerned, most of the examples in
the literature involve both static and dynamic sampling for atmospheric fluoride analysis. They are summarized in table 3. The French laboratories for some reason are content to just use one alkali coated filter paper in their dynamic air sampler. In Australia, the dual tape sampler has come into favour, method ASTM D3266, after years of just using the same single filter method as the French.

There is a growing body of literature on the principles and use of personal dosimeters. One type involves dynamic sampling with a small battery pack, air pump and gas badge (a coated material such as a filter paper or polymeric fibre), or a midget impinger. There is a trend toward passive dosimeters which are static sampling devices. The problem of dependance on air velocity is eliminated by a design which creates a static gas diffusion layer immediately next to the reactive surface.

9. General Discussion and Conclusions.

The value of the limed filter paper method is that it is simple, inexpensive and does not require attention during the exposure period. The dynamic methods require electricity at each sampling station and must be checked frequently as well as have filters exchanged. In section 3 we pointed out that the dynamic methods are often considered to require too much skill or they involve an apparatus which is not sufficiently rugged. These factors make the limed filter paper, static sampling method suitable for situations involving a preliminary area survey or a large number of permanent monitoring stations, particularly where the aim is to look qualitatively at trends in seasonal or annual fluoride exposure, and the normal levels are low. This is the philosophy at OME in the case of Port Hope. Area ground level atmospheric fluoride levels have been sufficiently low to be of potential concern mainly as to damage of vegetation. This is why OME and Eldorado use fluoridation index and don’t attempt to convert to atmospheric concentration. If notable excursions start to occur, then more sophisticated monitors can be put in place.
Values of fluoride deposition rate can be of qualitative value. At Port Hope the use of $V = 11 \text{ mm/s}$ would allow routine estimates of gaseous HF concentration within about $\pm 50\%$. Because the method is site specific it has not been possible to evaluate the precision of the limed filter paper method of fluoride collection. However due to variations in meteorological conditions during the sampling period, it is unlikely to be better than $\pm 50\%$. Under accident conditions, a precise knowledge of wind direction and speed, plus a calibration of the sample shelter's attenuation factor between wind speed and air velocity at the filter paper surface, would allow a more precise value of $V$ to be obtained from the data of Wilson et al in figure 1. In this way $\pm 20\%$ accuracy would be the best one could hope for, for constant wind velocity at the station. Note that if wind velocity falls but is assumed to be constant at the higher value, humans could receive a higher exposure than calculated from the observed deposition.

Low limed paper deposition rates do not necessarily mean a significant fluoride release to the atmosphere has not occurred. In addition to the possibility of a drop in wind velocity mentioned above, or a rainfall, uncertainty can arise from the integrating nature of the method and hence the reduction in apparent average exposure level, caused by prolonged sampling times and the assumption of constant fluoride level over the period.

The above effects, plus the poor (very low) results obtained with 30 day samples\textsuperscript{22} suggest that the latter are of little value for estimating atmospheric fluoride, or even for estimating fluoride exposure to vegetation. The latter purpose might be achieved with revised technique for preparing the limed paper\textsuperscript{22}. Failing that, then the provincial 30 day criteria should perhaps be measured against the sum of 30 daily - or 4.3 weekly samples.

A 24 hour sampling period, which gives a detection limit of 0.5
ug/m$^3$ (based on 5 ug/dm$^2$ and V = 11 mm/s), would be most useful in evaluating emissions (the station still must be downwind). This is because, just as for 30 day samples the 7 day sampling period causes a low result to be calculated for situations where the fluoride level is high only part of the time.

To increase the potential use of the limed paper technique under accident conditions a slightly more extensive network of sample stations would be needed to cover all wind directions (see figure 2). Even the 7 day samples would be useful if collected immediately following an accident. Little error would be introduced by the assumption that all the deposited fluoride arises from exposure at the time of the accident, especially if stack gas readings indicate normal emissions prior to the accident. The assumption of constant wind velocity must not be forgotten.

In the case of unusual stack gas emissions, and especially in the case of an accidental major release, the proximity of the plant and the town would enable a quick real time fluoride survey to be made with little difficulty. This would involve a unit mounted on a mobile van. For the van to cover the survey area in a short enough time, a fast response method of gaseous fluoride analysis would be required. Method ASTM D3267-80 (filter + impinger air collection, FSE analysis) requires 5 min. or so to reach steady state which would be too slow if a major accidental release has occurred.

For very fast response measurement of HF in air, the use of optical absorption laser techniques seems to offer the most promise. Bostick et al$^{15}$ mention the possibility and point out the potential problem of interference by CO$_2$ or water vapour. Use of a He-Ne laser at 2.4 um has been suggested for HF detection. However it is difficult to operate a He-Ne laser at 2.4 um wavelength and the method is too insensitive without the use of special techniques - 20 ug/m$^3$ for 500 m path length$^{54}$. 
However the use of a diode laser at 1.33 μm would allow measurement of an HF absorption overtone. The approach of Griser et al\textsuperscript{55} achieves a detection of 1 mg/m\textsuperscript{3} with a 1.2 m absorption path length. However simple diode laser modulation techniques\textsuperscript{56} should enable much better sensitivity.

Inexpensive, simple to operate, optical communication diode lasers operating at 1.3 μm are commonly available and are being studied by Prof. Dan Cassidy (McMaster University, Dept. of Engineering Physics) for application as air pollutant detectors. In conjunction with a high speed air pump and a multireflection gas cell, a mobile high sensitivity, fast response, real time HF analyser may be feasible. The devices are cheap enough to possibly install a network of permanent monitoring stations.

In conclusion, some of the limed filter paper data may be useful in roughly estimating atmospheric fluoride concentration or fluoride exposures under both routine and accident conditions. However the data must be treated with considerable caution. The 30 day samples, and even the 7 day samples are of less potential value than the 24 hr ones.

The technique of preparing limed papers should be reviewed.

The use of personal HF dosemeters for employees should be considered.

Consideration should be given some research on the possible use of a 1.3 μm wavelength optical communication type diode laser for HF monitoring in real time. Consideration should also be given to a mobile HF detection unit for fast area surveys following unusual or major accident emissions.

The more important recommendations are highlighted in table 10.
### COMMON HYDROGEN FLUORIDE SOURCES.

- alumina reduction
- combustion of coal
- phosphate fertilizer, $H_3PO_4$ production
- HF production
- clay based products
- glass manufacture
- steel manufacture
- phosphate mining
- $UF_6$
- volcanoes
### Table 2

**Ontario Fluoride Regulations**

<table>
<thead>
<tr>
<th>Substance</th>
<th>Time</th>
<th>Standard</th>
</tr>
</thead>
</table>
| Gaseous fluoride (as HF)                   | April 15-Oct.15 | 0.86 ug/m³ (24 hours)  
                                           |               | 0.34 ug/m³ (30 days)       |
| Total fluoride (gaseous and particulate)   | April 15-Oct.15 | 1.72 ug/m³ (24 hours)  
                                           |               | 0.68 ug/m³ (30 days)       |
|                                           | Oct.16-April 14 | 3.44 ug/m³ (24 hours)  
                                           |               | 1.38 ug/m³ (30 days)       |
| Fluoride in forage (dry weight)            |               | 35 ppm   |
| Fluoridation index*                        | April 15-Oct.15 | 0.4 ug/cm²/30 days  
                                           |               | or 0.0133 ug/cm²/day       |
|                                           | Oct.16-April 14 | 0.8 ug/cm²/30 days   
                                           |               | or 0.0266 ug/cm²/day       |

*Fluoridation index is the weight of total fluorides (in micrograms) collected by 100 sq. centimetres of limed filter paper in 30 days.

### Table 3

**Canadian Federal Fluoride Standards (Objectives)**

<table>
<thead>
<tr>
<th>Standard</th>
<th>Time</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.85 ug/m³</td>
<td>for 24 hours (Fₘ)</td>
</tr>
<tr>
<td>0.55 ug/m³</td>
<td>for 7 days (Fₘ)</td>
</tr>
<tr>
<td>0.35 ug/m³</td>
<td>for 1 month (Fₘ)</td>
</tr>
<tr>
<td>0.20 ug/m³</td>
<td>for 70 days (Fₘ)</td>
</tr>
<tr>
<td>0.40 ug/m³</td>
<td>for 24 hours (Fₘ)</td>
</tr>
<tr>
<td>0.20 ug/m³</td>
<td>for 7 days (Fₘ)</td>
</tr>
</tbody>
</table>
Table 4

CONVERSION FACTORS.

<table>
<thead>
<tr>
<th>Units of Deposition Rate</th>
<th>Conversion Factors to ug/m²/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>ug/m²/s</td>
<td>x 1</td>
</tr>
<tr>
<td>ug/dm²/day</td>
<td>x 1.16 x 10⁻³</td>
</tr>
<tr>
<td>ug/dm²/week</td>
<td>x 1.65 x 10⁻⁴</td>
</tr>
<tr>
<td>ug/dm²/30 day</td>
<td>x 3.86 x 10⁻⁵</td>
</tr>
<tr>
<td>ug/cm²/30 day</td>
<td>x 3.86 x 10⁻³</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Units of V</th>
<th>Conversion Factor to m/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>m/s</td>
<td>x 1</td>
</tr>
<tr>
<td>mm/s</td>
<td>x 10⁻³</td>
</tr>
<tr>
<td>ug/dm²/ppm min</td>
<td>2 x 10⁻³</td>
</tr>
<tr>
<td>ug/dm²/day/ppb</td>
<td>1.4 x 10⁻³</td>
</tr>
<tr>
<td>m⁻³/dm²/day</td>
<td>1.16 x 10⁻³</td>
</tr>
</tbody>
</table>

Sample Calculation of Atmospheric HF: (see section 6)

40 ug/dm²/day, x100 -> 4000 ug/m²/day, - 24 (day -> hr.) and - 3.6 x 10³ (hr. -> sec.) giving 0.046 ug/m²/s; - V=0.011 m/s gives HFg= 4.2 ug/m³.

Table 5

CALIBRATION METHODS

France - single filter

ASTM

D3266-79 dual tape (dual filter (OME))

D3267-80 filter + impinger

D3268-85 NaHCO₃ coated tube + filter

D3269-79 FSE (fluoride selective electrode) analysis
### TABLE 6
EFFECT OF AIR VELOCITY

<table>
<thead>
<tr>
<th>Reference</th>
<th>Air Velocity m/s</th>
<th>$\sqrt{V(m/s)}$</th>
<th>V mm/s</th>
</tr>
</thead>
<tbody>
<tr>
<td>32</td>
<td>1.33</td>
<td>1.15</td>
<td>26.6</td>
</tr>
<tr>
<td></td>
<td>2.22</td>
<td>1.5</td>
<td>33.2</td>
</tr>
<tr>
<td></td>
<td>4.44</td>
<td>2.1</td>
<td>43.6</td>
</tr>
<tr>
<td>31</td>
<td>1</td>
<td>1</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>2</td>
<td>59.8</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>2.8</td>
<td>94.5</td>
</tr>
<tr>
<td>Air Sampling Method</td>
<td>Fixant</td>
<td>Geometry</td>
<td>Shelter</td>
</tr>
<tr>
<td>---------------------</td>
<td>--------</td>
<td>----------</td>
<td>---------</td>
</tr>
<tr>
<td>static CaO</td>
<td>12.5 ca dia.</td>
<td>box</td>
<td>open floor &amp; soffit both sides</td>
</tr>
<tr>
<td>static CaO</td>
<td>9 sq. dm</td>
<td>vertical cylinder</td>
<td>yes, no details</td>
</tr>
<tr>
<td>static NaOH</td>
<td>9 sq. dm</td>
<td>vertical cylinder</td>
<td>yes, no details</td>
</tr>
<tr>
<td>static NaOH</td>
<td>6.96 sq.cm</td>
<td>dish wall</td>
<td>vertical</td>
</tr>
<tr>
<td>static CaO</td>
<td>11 ca dia.</td>
<td>double louvered</td>
<td>vertical screen</td>
</tr>
<tr>
<td>static CaO</td>
<td>glass fibre</td>
<td>dish well</td>
<td>on 4.8 cm dia. Petri dish, inverted one side</td>
</tr>
<tr>
<td>static CaO</td>
<td>12.5 ca dia.</td>
<td>V-roof</td>
<td>open side</td>
</tr>
<tr>
<td>static K2CO3</td>
<td>5 cm dia.</td>
<td>a) double louvered screen</td>
<td>both sides</td>
</tr>
<tr>
<td>static K2CO3</td>
<td>5 cm dia.</td>
<td>b) none</td>
<td>a) 0.3</td>
</tr>
<tr>
<td>static CaO</td>
<td>0.7 sq. dm</td>
<td>none</td>
<td>f.p. at f.p. surface</td>
</tr>
<tr>
<td>static CaO</td>
<td>0.7 sq. dm</td>
<td>cylinder</td>
<td>vertical outer surface</td>
</tr>
</tbody>
</table>
Table 8

**VARIATIONS IN TECHNIQUE.**

- amount of fixant
- type of fixant
- size of paper
- shape of paper
- orientation
- type of shelter

Table 9

**MAIN FACTORS RESTRICTING USE.**

- $\text{F}$ loss from 30 day exposure

- knowledge of wind velocity and direction and possible changes during sample period (value of $V$)

- knowledge of shelter effect on air velocity at filter paper surface (value of $V$)

- perturbations by buildings

- $\text{F}$ uptake by vegetation

- insensitive to particulates, especially $\text{UO}_2\text{F}_2$

- rain

- effect of prolonged sampling time on calculated value of $[\text{HF}_g]$
RECOMMENDATIONS.

- do not use 30 day exposures (F loss, artificial reduction in answer) to calculate $HF_g$

- improve filter paper preparation

- consider adding a few more stations

- emphasize 24 hr. data but caution in evaluating $[HF_g]$ as wind can vary

- consider mobile rapid response unit (re large releases)

- consider personal dosemeters
FIGURE 1: Effect of air velocity on limed filter paper uptake of HF from the atmosphere
FIGURE 2: Map of Port Hope, Ontario with the location of Eldorado Resources Ltd.'s limed filter paper stations for static sampling of atmospheric fluoride.
References.


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