FUGITIVE EMISSIONS OF A PVC POLYMERISATION UNIT : EXPERIMENTAL EVALUATION

Authors : MM. J.-P. BINDELLE (SOLVAY S.A., Brussels)
P. DEPRET (SOLVAY S.A., Tavaux Plant, France)

VCSA meeting, oct. 6th & 7th, 1993.

ABSTRACT : Experimental data on fugitive emissions of a PVC plant show that fugitive VCM emissions are orders of magnitude lower than controlled emissions. THe figures are also much lower than those based on the emissions factors published in the literature for petrochemical industry. The low emission value in PVC polymerisation is probably due to the traditional high standards used for leakage reduction, aiming to reduce the exposure of personnel to vinyl chloride. The potential reduction of emission by the possible substitution of conventional valves by bellow valves is negligible.

1. SCOPE OF THE STUDY

Atmospheric emissions of petrochemical plants consist of three parts :

- controlled emissions : normal exhaust gases of the process, scheduled opening of equipment,...
- accidental emissions : abnormal emissions of the Pressure Safety Valves (PSV) and other equipment in case of emergency
- fugitive emissions : emissions arising from potentially leaking equipment (valves, flanges, pump seals, compressors, pressure relief valves,..., see appendix 1)

Controlled emissions are rather well known. Optimisation of the process and of the operating procedures allow to keep them into acceptable limits.

Safety measures and procedures reduce frequency and amount of such **accidental emissions** to very low values.

Fugitive emissions are difficult, indeed even impossible to quantify in all cases. Industry applies "Codes of Good Practice" to reduce them as much as possible. They are :

- associated with volatil organic compounds potentially present at numerous points throughout a petrochemical manufacturing unit,
- randomly dispersed according to various parameters : age and type of equipment used, maintenance programs,...

Measurement or estimation of the actual of fugitive emissions in global atmospheric emissions of a chemical unit is rather difficult and extremely expensive. For petrochemical industry in general some authors believe that they could represent between 30 and 70 % of the total air emissions [1,4,10].

Emission factors associated with the type of equipment and the level of screening values (portable leak detectors ["sniffers"] near potentially leaking equipment) have been proposed by different authors (leak-no leak method, stratified factors, correlated factors [1,2,3,6]; see appendix 2).

The range of factors is quite large (for instance 1 to 100 g/h for valve handling lights liquids [4]). The origin of such disparity is due to many factors : maintenance, conception, preventive procedures, ... [8,10].

Different studies achieved in chemical units show that conventional emission factors used can lead to large overestimations [8,13,14].

Overestimated fugitive emissions will likely generate negative public perception.

PVC industry, who faced with the ASL problem in 1974, took impresive measures (equipment upgrade, process improvements, special procedures, organization,...) to reduce drastically exposure of personnel to VCM, reducing at the same time controlled and fugitive emissions.

For these reasons one may presume that the level of fugitive emissions is probably much lower in PVC industry than in common petrochemical industry.

In 1992 SOLVAY went into an experimental study of a PVC polymerisation unit of the Tavaux PVC plant (France), in order to verify the veracity of the assumption, and to give an estimate of the fugitive emissions of the unit compared with controlled emissions.

2. MATERIAL AND METHODS

2.1. Description of the studied area

The studied volume is a closed polymerization room of 580 m^3 located at 16 m heigth (appendix 3). It contains the top part of two 120 m^3 reactors producing suspension PVC according to the closed process technology. We took advantage of this particularity to perform the measurement program.

This plant has been erected at the end of the seventies using the best available technology and has been operated with skilled people applying strict operating and maintenance procedures to reduce fugitive emissions (see the "Code of good practice" proposed by ECVM [12]).

The studied volume contains about 2/3 of the critical equipment (manifold, pneumatic valves, flanges, manual valves, end-line caps,...) associated with liquid VCM transfer in the unit.

The air is extracted from the polymerization room by 4 air fans running constantly (3000 m^3/h each).

2.1 Measurement techniques

A rigid cardboard section of about 2 m lenght was adjusted in front of fan propeller to enable sampling in a pseudo isokinetic way (appendix 4). The sampling location and the actual flowrate were checked by measurement of the speed of the air lines across the section (Note : due to their quick diffusion isokinetic sampling is not requested by usual standards for volatil organic compounds gases).

From the head of one reactor a known amount of the of tracer gas (SF6) was released at a constant rate and recovered regularly (vacuum bottles) at sampling location to estimate the actual flowrate of the ventilation system.

Analysis of SF_6 were performed on a FID CHROMPACK P9000 gas chromatograph equipped with column DB1301 of 60 m, film thickness 1 μm).

VCM was collected at each fan by a SIPIN Personal Sampler Pump SP1 (0.5 dm^3/h) through adsorption cartridge (PERKIN ELMER ATD50 of 1 cm^3). During the first trial, 4 different pumps using different flowrates (0.25-0.50 dm^3/min) and sampling duration (20, 30 and 50 min) were used on one of the fan in order to control the sampling conditions.

The mesurements were performed three times during running periods of 4 up to 6 hours (total 129 samples taken).

Analysis of VCM adsorbed were achieved by chromatographic analysis on FID (Flame Ionization Detector) PERKIN ELMER ATD50 equipment (detection level of 0.5 $\mu l/m^3$ for a sampling period of 8 hours, i.e. 2.5 ppb).

The level of VCM was also monitored by the fixed system (GC FID CARLO ERBA serie 1000) normally used for the continuous control of hygiene at workplace, and by 8 passive cartridges (open end without pump) located at each 1/8 of the unit and adsorbing during the whole sampling period.

2.3 Bagging measurements

In order to quantify the leak rate of some individual equipment, some bagging trials were achieved by isolating the equipment with a triple layer (PEHD/Al/PEHD) sheet (CLARYL, RHONE POULENC LYON).

The air tight tent was purged with dry air to control any loss of pressure, then emptied by a vacuum pump, and filled again with dry air; sample was taken after a defined period of equilibrium with the tested equipment.

3. RESULTS

3.1 Flowrate and replacement rate of the extract air

The air speed in the sampling section vary from 5.3 to 5.9 m/s and is not symetric. The air flowrate extracted by each fan is 3630 m3/h (average value) with standard deviation of 895 m3/h.

The measured replacement rate is about 25 times/hour.

The sampling was located at the point where a mean velocity was measured.

3.2. Tracer gas

94 % of the emitted tracer was identified in the measurements, 97 % at the two fans located near the reactor where the tracer was emitted (appendix 5).

Concentration of SF_6 decreases rapidly after the end the injection. All those facts lead to conclude that : ventilation system is very efficient and measurements on relatively short periods reflect the actual variations in the emissions rates. Moreover, cross contamination between the two reactors heads and samples was shown insignificant.

3.3. VCM measurements

VCM concentration varies from 5 to 50 $\mu l/m^3$ (see an example in appendix 5). The comprehensive emission computed on these values is 0.7 g/h in average or 6 kg/year. Related to production, such emission is < 0.1 g/t_{PVC}, to be compared with some tens g/t of controlled emissions.

This very low value was measured in the plant working at full capacity (without incident during the trials). (Remark : in case of leakage, detected by the continuous GC CARLO ERBA, a correction procedure is applied by the operators to restablish the normality).

Considering the chronologic evolution of the measured emissions according to the different polymerization conditions, it can be observed that VCM emission increases with some operations like filling, emptying, degassing, ...

For instance, the average concentration increases from about 10 $\mu l/m^3$ (base level) to 50 $\mu l/m^3$ during VCM introduction.

When considering the number of pneumatic valves (in contact with VCM) actuations during the sampling periods one can estimate that VCM release is approximately :

- 5O mg/valve.hour, or
- 25 mg/actuation.

3.4. Consistency with the continuous GC monitoring

During the 3 sampling periods, practically no usable peak was observed by the continuous chromatograph (detection level = 0.1 ppm) : this is consistent with measured levels.

3.5. Consistency with the fixed passive samplers

The average level measured by the fixed passive samplers (35 $\mu l/m^3$) gives an estimate of total emissions ($\approx$ 1.3 g VCM/h) higher but consistent with SIPIN measurements.

3.6. Consistency with bagging measurements - Emission factors

The above actual emissions values are very low and we would like to confirm them by spot bagging measurements several times on three typical equipments handling liquid VCM : one flange, one manual valve and one automatic valve.

Bagging measurements are very expensive and the aim was not to perform a exhaustive statistical study but to to check if the emissions factors of the equipment were consistent with the low emission measured (see appendix 7).

The emission factor for the flange (SUPRANITE OIL gasket of SIEM) is 30-40 μg/h.

For the manual valves the range observed is between 300 and 1400 μg/h.

The automatic valve (TUFLIN without bellow) has an emission factor varying from 2μg/h in stand-by to 10 mg/h in operation. The result confirms publications in the literature [11] saying that bellow valves are not essential to reduce fugitive emissions.

Compared with published results, the values measured by SOLVAY are very low and confirm DOW data on Chlorine emissions [13]. They are **consistent** with the low emission figures in the area.

An explanation of the good results can be the preventive maintenance procedure and the criterion for intervention. Years ago US procedures recommanded repairs (for safety reasons) when the "OVA" detected more than 10000 ppm at one point of the leaking device. More recently EPA lowered the recommandation to 500 ppm.

At this SOLVAY Tavaux plant, 230 critical points are checked monthly and the intervention level for maintenance is 20-50 ppm.

4. CONCLUSIONS

Although the study is not exhaustive (2/3 of the critical material was checked, no incident during measurement, number of experiments,..), consistency and very low figures lead to following conclusions :

- The level of **fugitive emissions** is significantly **lower** than the level of **controlled emissions**. This results justifies fully ECVM recommandations for reduction of fugitive emissions [12].

- The actual level of emissions shows that potential reduction by the possible substitution of conventional valves by **bellow valves** is negligible.

- The best available technology and the **Code of good practice**, both proposed by ECVM, give for PVC industry lower level of emission than those usually admitted by the literature for general petrochemical industry. In particular, preventive monitoring of fugitive emissions and good maintenance by skilled people is a suitable practice which keeps **fugitive emissions** at a **very low** and acceptable level.

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Proportion des équipements présentant des taux d'émissions significatifs (càd > à 0.5 g/h) en % du n total d'équipements selon [1]

Equipement	industrie oxyde éthylène	industrie butadiène	raffineries pétrole	
vannes	4.5	15	13	
garnitures de pompes	16	39	36	
garniture compresseurs	50	95	54	
clapets de sécurité	0	36	23	
brides	3	0	1	

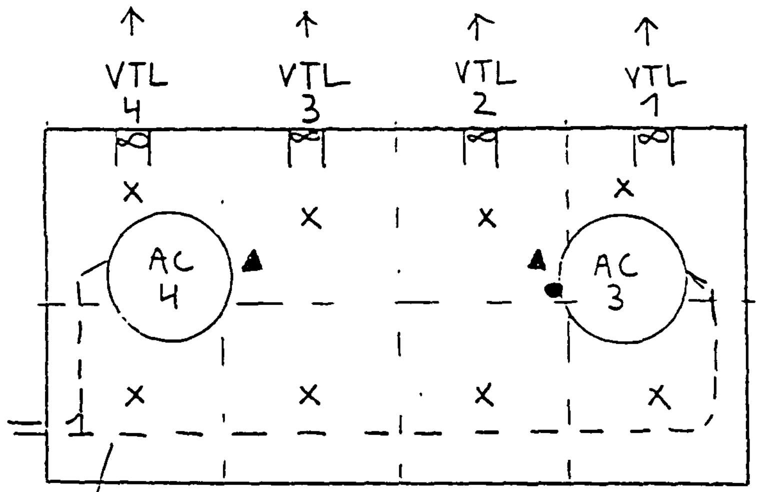
Emissions atmosphériques fugitives.
Comparaison des facteurs d'émission selon diverses sources en g.h−1.source−1

	selon SCHAICH, 1991					selon BERGLUND et al	
Equipement	SOCMI [1]	L > 10000 [2]	NL < 10000 [3]	facteurs stratifiés 1000à10000 [4]	0 à 1000	ind C2H40 [5]	[6]
vannes gaz	5.6	45.1	0.48	1.65	0.14	0.2	0.22
vannes liq légers	7.1	85.2	1.71	9.63	0.28	0.25	0.63
vannes liq lourds	0.23	0.23	0.23	0.23	0.23		
garnitures pompes							
liquides légers	49.4	437	12	33.5	1.98	19.4	19.4
liquides lourds	21.4	389	13.5	92.6	3.8		
garnitures de compresseurs gaz/vap	228	1608	89.4	264	11.3	0.35	0.35
clapets de sécurité gaz/vapeur	104	1691	44.7	279	11.4	0.07	0.07
brides	0.83	37.5	0.06	8.75	0.02	0.25	0.32
bouche−trous	1.7	11.9	1.5	8.8	0.13	0.49	0.49
prises échantillons	15	12	1.5	−	−	−	−

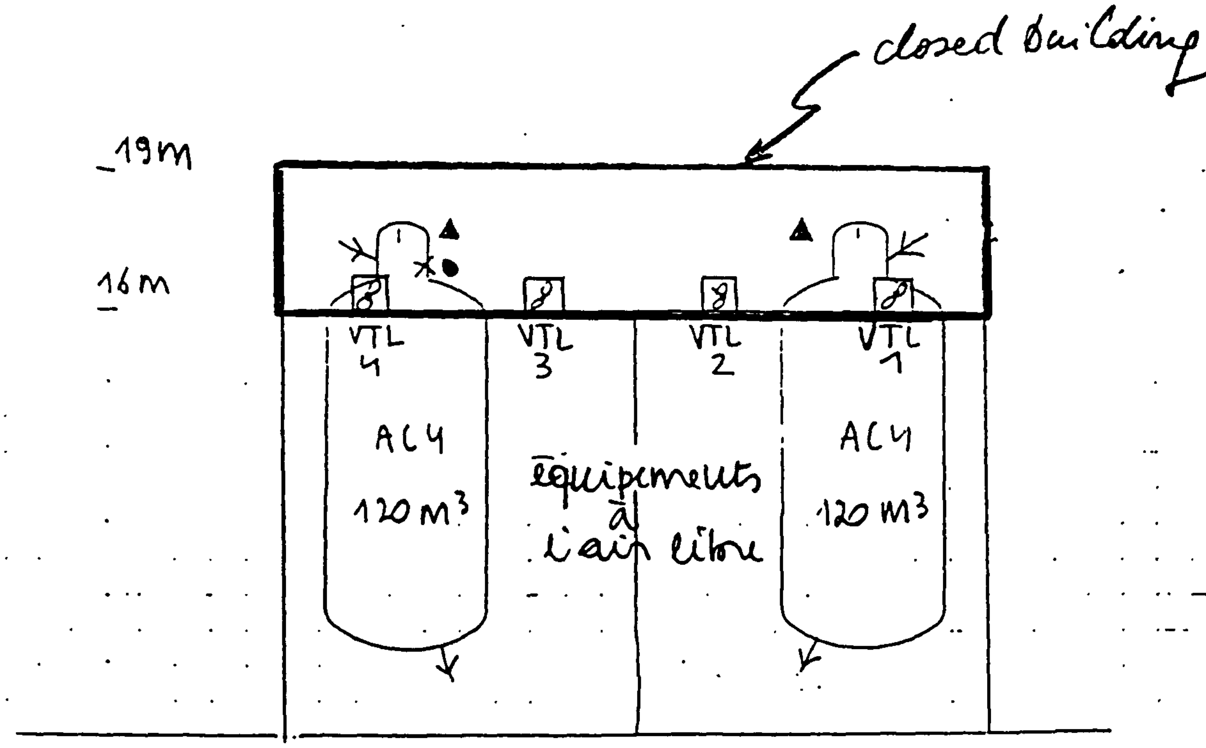
[1] facteurs SOCMI (recommandés par la Society of Organic Chemicals Manufacturing Industry)
[2] facteurs applicables aux sources considérées comme fuyardes (L) (contrôle analyseur > 10 000 ppm)
[3] facteurs applicables aux sources considérées non fuyardes (NL) (contrôle analyseur < 10 000 ppm)
[4] facteurs stratifiés (contrôle analyseurs 0−1000 ppm, 1000−1000 ou > à 10000 cfr [3])
[5] facteurs moyens mesurés dans l'industrie de l'oxyde d'éthylène
[6] facteurs tenant compte d'une concentration "par défaut" lors du contrôle des équipments de 8 ppm

CTL015375

Implantation des AC, VTL et des points de mesure



alimentation en VC liquide et chargement AC



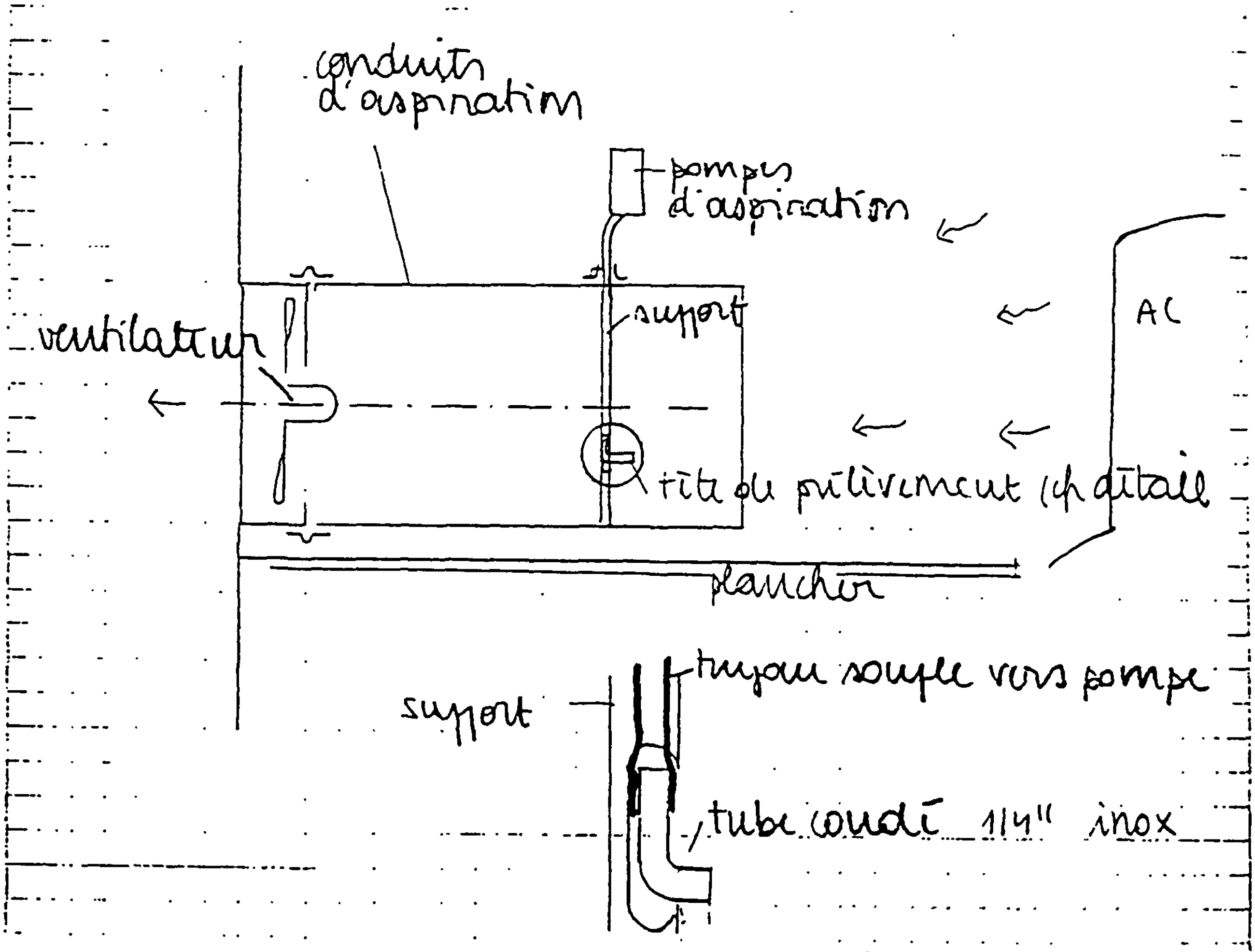
● point d'injection du SF6 dans l'air

▲ sondes VCM reliées au chromato continu

☐ ventilateur d'extraction — conduits ajoutés

× point de prélèvement poste fixe

Implantation des têtes de prélèvement des pompes dans les conduits d'aspiration des VTL



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MESURE DES EMISSIONS FUGITIVES P79
ESSAI DE TRACAGE AU SF6 DU 27.2.1992

résultats exprimés en µl SF6.m−3

	HEURE	VTL1	VTL2	VTL3	VTL4
	11h00m	début injection SF6			
	11h20m				
	11h40m				
	12h00m	70	20	<10	<10
	12h20m	100			
	12h40m	140			
	12h45m		20		
	13h00m	280		20	
	13h20m	250			
	13h30m		170		
	13h40m	110			
	14h00m	370		<10	<10
	14h15m		25		
	14h20m	170			
	15h00m	110	40	10	
	15h20m	30			
	15h40m	65			
	15h45m		<10		
arrêt	16h00m	35		<10	<10
	16h20m	<10			
	16h30m		<10		
	16h40m	<10			
	17h00m	<10		<10	
	17h10m	<10			
	17h15m		<10		
	17h20m	<10			

moyenne pendant durée effective de traçage (12:00 à 16:00)

MOY 4VTL	VTL1	VTL2	VTL3	VTL4
49	144	46	6	0
UNE MESURE EN POSTE FIXE (C6)				15

SECTION 0.196 m2

débit d'air extrait par VTL (m3/h)					TOTAL
NOMINAL	3500	3500	3500	3500	14000
MESURE					3534.3

quantité de SF6 extraite par les VTL					TOTAL
en µl.m−3	505	160	21	0	686
en g	14.1	4.5	1.5	0.0	20.0
soit en %	*74*	*23*	*3*	*0*	*100*

masse SF6 émise (pesée de la bouteille) 21.4 g

% de récupération : 94 %

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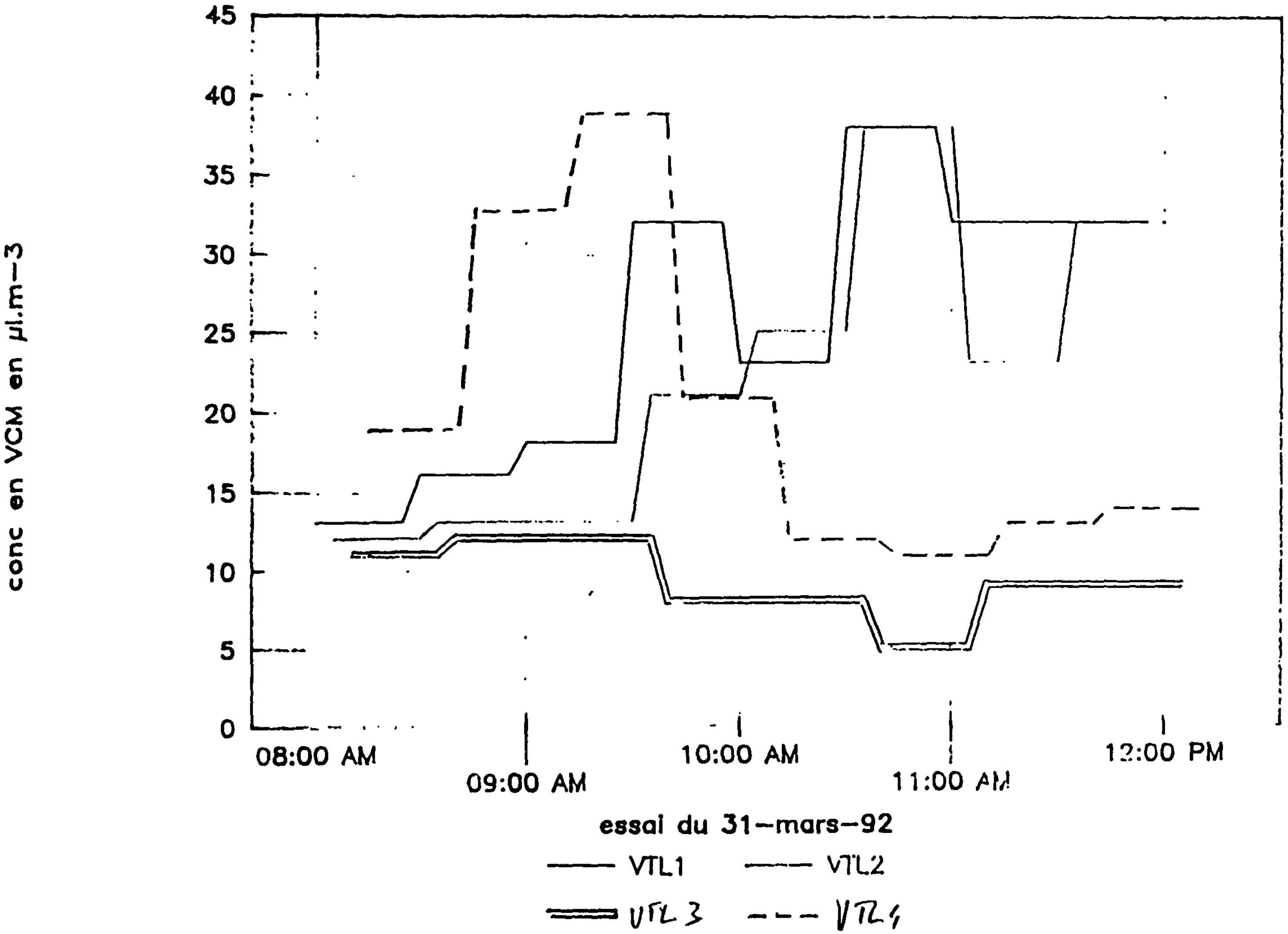
MESURES DES EMISSIONS FUGITIVES

VCM extrait par les 4 VTL



APPENDIX 5

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SOLVAY
USINE DE TAVAUX
SERVICE ENVIRONNEMENT

MESURE DES EMISSIONS FUGITIVES SUR DIVERS EQUIPEMENTS

DATE	TYPE D'APPAREIL	TEMPS EQUILIBRE [heure]	VOLUME EMBALLE [dm3]	CONCENT EN VC1 [ml.m−3]	DEBIT DE FUITE [µg.h−1]
21−Avr−92	bride VC liquide	2.00	1.3	18	33
22−Avr−92	bride VC liquide	2.08	1.2	26	42
23−Avr−92	bride VC liquide	16.67	0.9	259	39
28−Avr−92	vanne autom [1]	0.75	2.75	342	[3] 3499
28−Avr−92	vanne autom [2]	16.3	2.5	< 5	< 2.1
30−Avr−92	vanne manuelle	18.33333	10	193	294
05−Mai−92	vanne manuelle	17	45	191	1411
06−Mai−92	vanne manuelle	41	40	370	1007

[1] une manoeuvre effectuée pendant la durée de mesure
[2] aucune manoeuvre effectuée pendant la durée de mesure
[3] 10 mg/h at full charge

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