



**PETes AA ANALYZER: AN INNOVATIVE INSTRUMENT
ALLOWING THE ONLINE MEASUREMENT
OF AA CONTENT IN PET PREFORMS**

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Outline

1. The idea
2. The traditional AA test
3. PETes AA analyzer: the operating principle
4. The study
 1. calibration
 2. method optimization
 3. correlation between PETes AA analyzer and traditional HS
5. How to do the test: a dedicated software
6. Advantages and benefits
7. Future innovation
8. Off-line and on-line version



The idea



Develop an automatic and fast system to measure the AA content in PET preforms.

Targets:

1. Reduce the lag time in giving the AA results, and thus increase the process control and monitoring
2. Simplify the AA test
3. Obtain reliable results
4. Allow on-line and off-line control
5. Reduce the costs of the AA test





The traditional test

Principle

Based on a gas chromatography analysis of the acetaldehyde present in head space, desorbed from ground material placed into a sealed vial after thermal treatment

Standard approach

- sample preparation
 - sample cutting
 - cryogenic treatment
 - cryogenic milling
 - weight a note quantity of sample in vial
- preparation of the calibration solution (acetaldehyde distillation and tritration)
- gas chromatography head space analysis (AA calculation by ISTD or ESTD)





The traditional test

Main variables

1. milling
 1. different sieves
 2. different cryogenic treatment
 3. different part of sample under testing (all or partial preform)
2. incubation time
3. sample conditioning temperature
4. different column and head space systems
5. different technician/individual





The traditional test

Data comparison

tests were performed on preforms from the same cavity (consecutive shots)

Methods	average value (ppm)
Independent laboratory internal test ⁽¹⁾	3.5
ASTM test ⁽²⁾	6.9
French Nat. test. ⁽³⁾	7.1
PDC internal test (according to UNI U590B2700) ⁽⁴⁾	3.7

Test condition

(1) 150°C-20 minutes

(2) 150°C-60 minutes

(3) 150°C-60 minutes

(4) 140°C-90 minutes



The traditional test

Data comparison

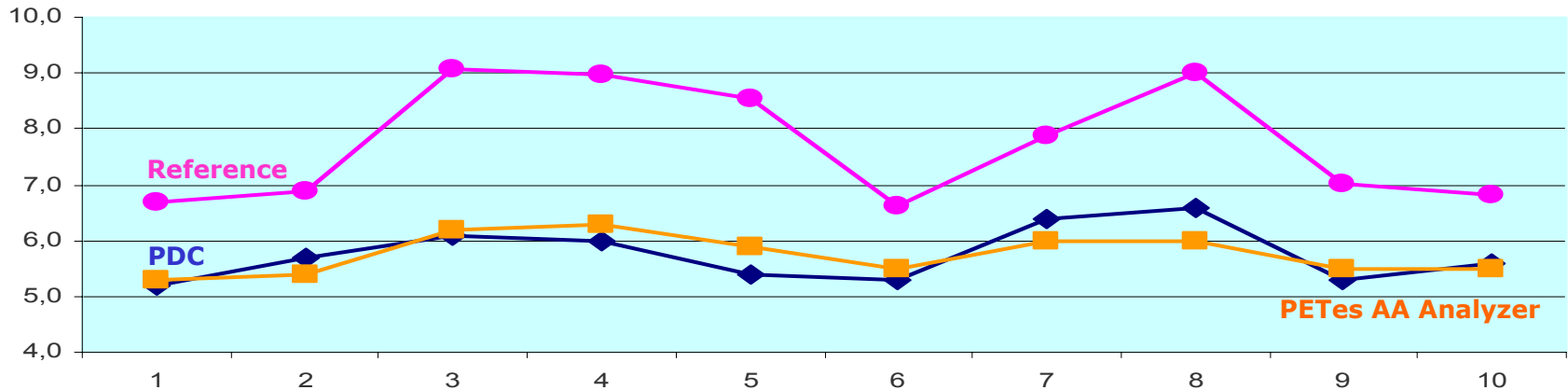
Average values (ppm) - 3 consecutive shots			
cavity	PDC (1)	Reference (2)	AA analyser (3)
1	5,20	6,68	5,30
7	5,70	6,89	5,40
10	6,10	9,07	6,20
18	6,00	8,96	6,30
20	5,40	8,53	5,90
24	5,30	6,63	5,50
27	6,40	7,87	6,00
38	6,60	9,01	6,00
42	5,30	7,02	5,50
45	5,60	6,82	5,50

Sample conditioning

(1) Tested by PDC, 140°C-90 minutes

(2) Reference, 150°C-60 min

(3) Tested by PDC using PETes AA analyser, 140°C-30 minutes





The traditional test

Critical factors to be considered in AA traditional measurements

1) difficulty in data comparison

It is just difficult to have a good repeatability (it is more difficult to talk about a reproducibility), taking in account also the variables coming from the injection process.

2) many variables in the methods

This is due to that, simply, changing some method parameters (heating temperature, incubation time, ...) or having different approach in the sample preparation (cryogenic mill, type of sieve, single or double milling, different technician, ...) it is **quite always** possible to correlate the results, but it is improbable to have the same results.

3) many different methods

There are a lot of methods, more or less official, and so on the same preform you can have different data. Which is the real data? In theory, no one is real, all are relative to the method use.

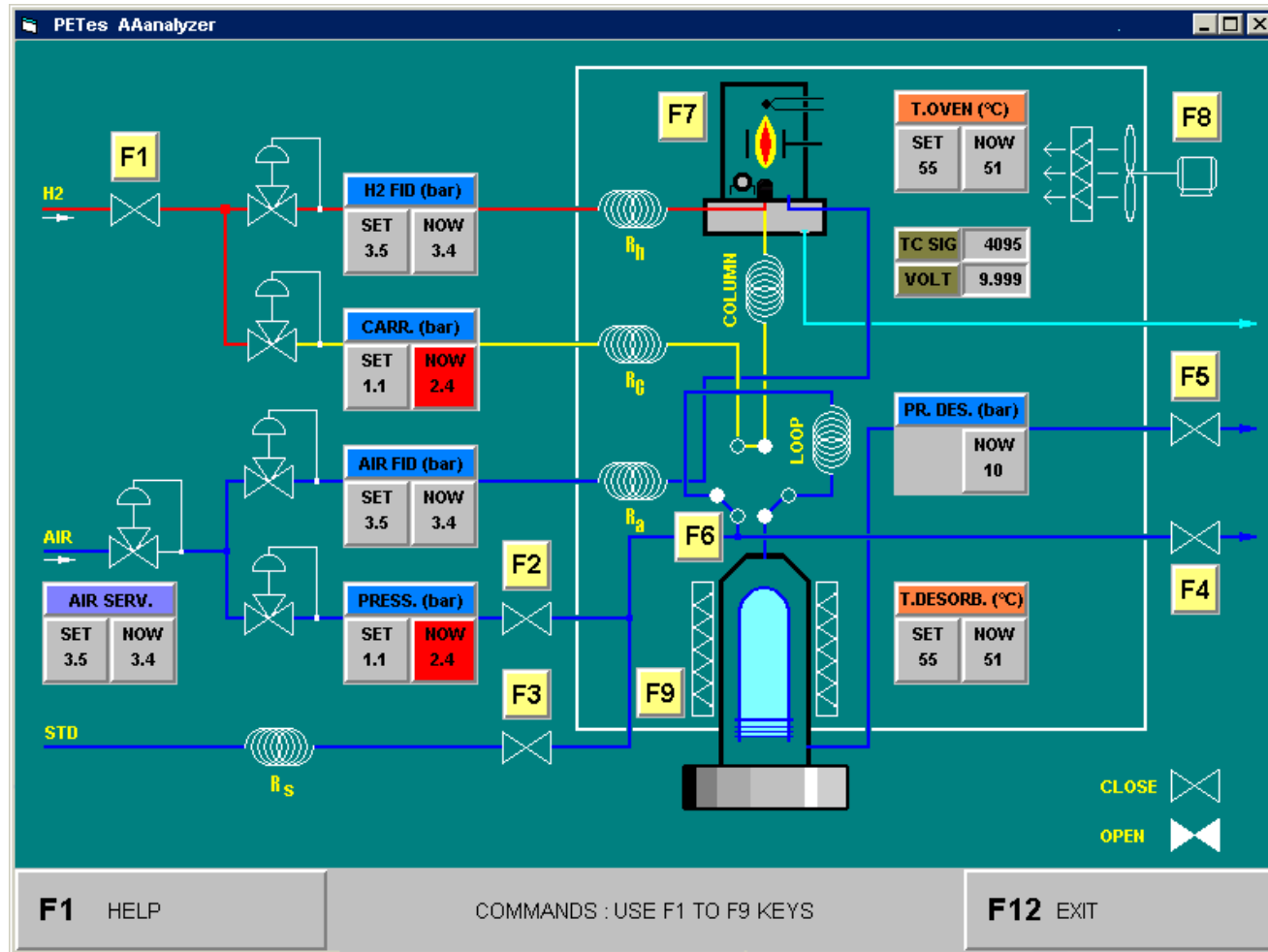


The operating principle

Based on the new Fast Head Space Gas Chromatography Technology.

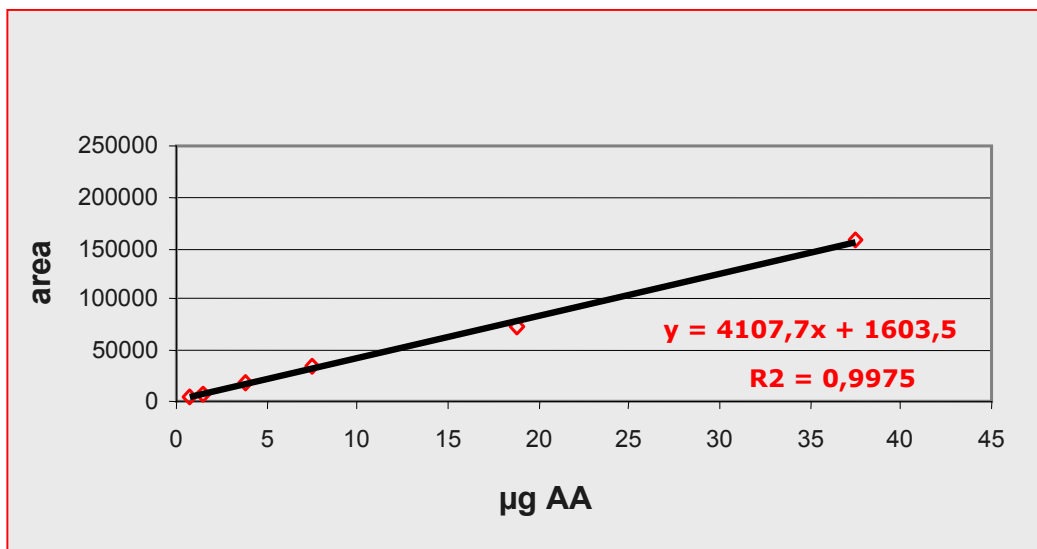
Operating Phases:

1. Washing
2. Sample conditioning
3. Pressurization
4. Load of the loop
5. GC analysis



Calibration

The calibration of the de-adsorption cell can be done by using a standard solution of AA in water, or using a solution of ethanol in water.



uL STD 7,5 g/l	AA ug	Area
0.1	0.75	4686
0.2	1.5	7851
0.5	3.75	18826
1	7.5	33809
2.5	18.85	73327
5	37.5	158048

Repeatability

	p1	p2	p3	p4	p5	p6	Average	SD	RSD%
7,5 ug	34475	32645	34306	34003	33793	34298	33920	671	1.98



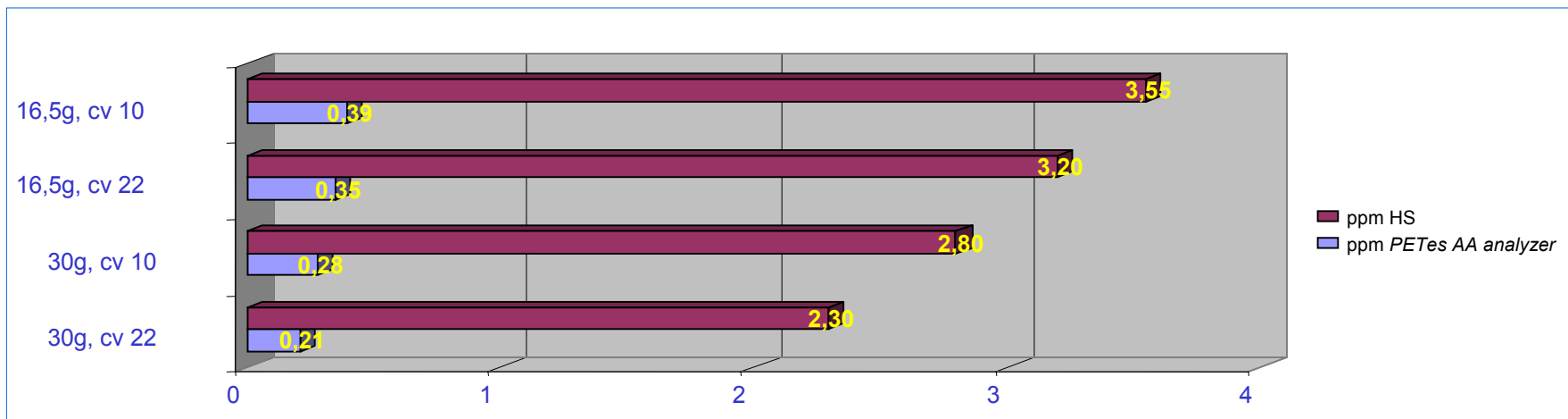


First Output

Data comparison

preform	PETes AA Analyzer Average value (ppm)	Traditional HS Average value (ppm)
30g - cv 22	0.21	2.30
30g - cv 10	0.28	2.80
16,5g - cv 22	0.35	3.20
16,5g - cv 10	0.39	3.55

Cavity 10/22		
	16,5	30
THS	1,11	1,22
PETes	1,11	1,33

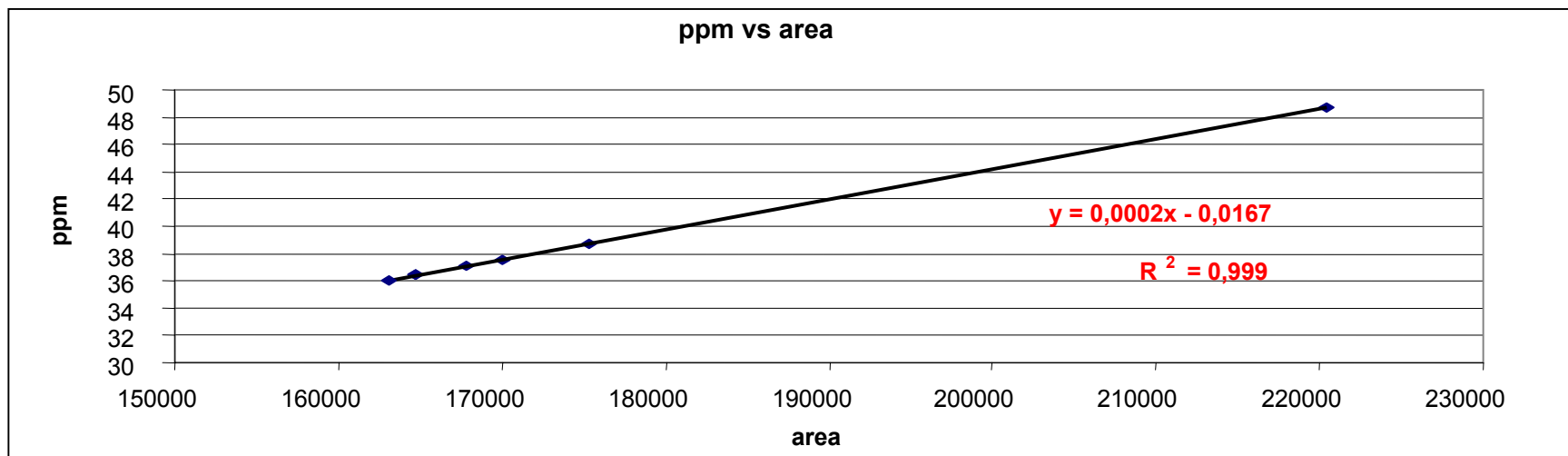




PETes method optimisation

Volume

According to the influence of the volume in head space analyses, a K factor has been determined for the de-adsorption cell.

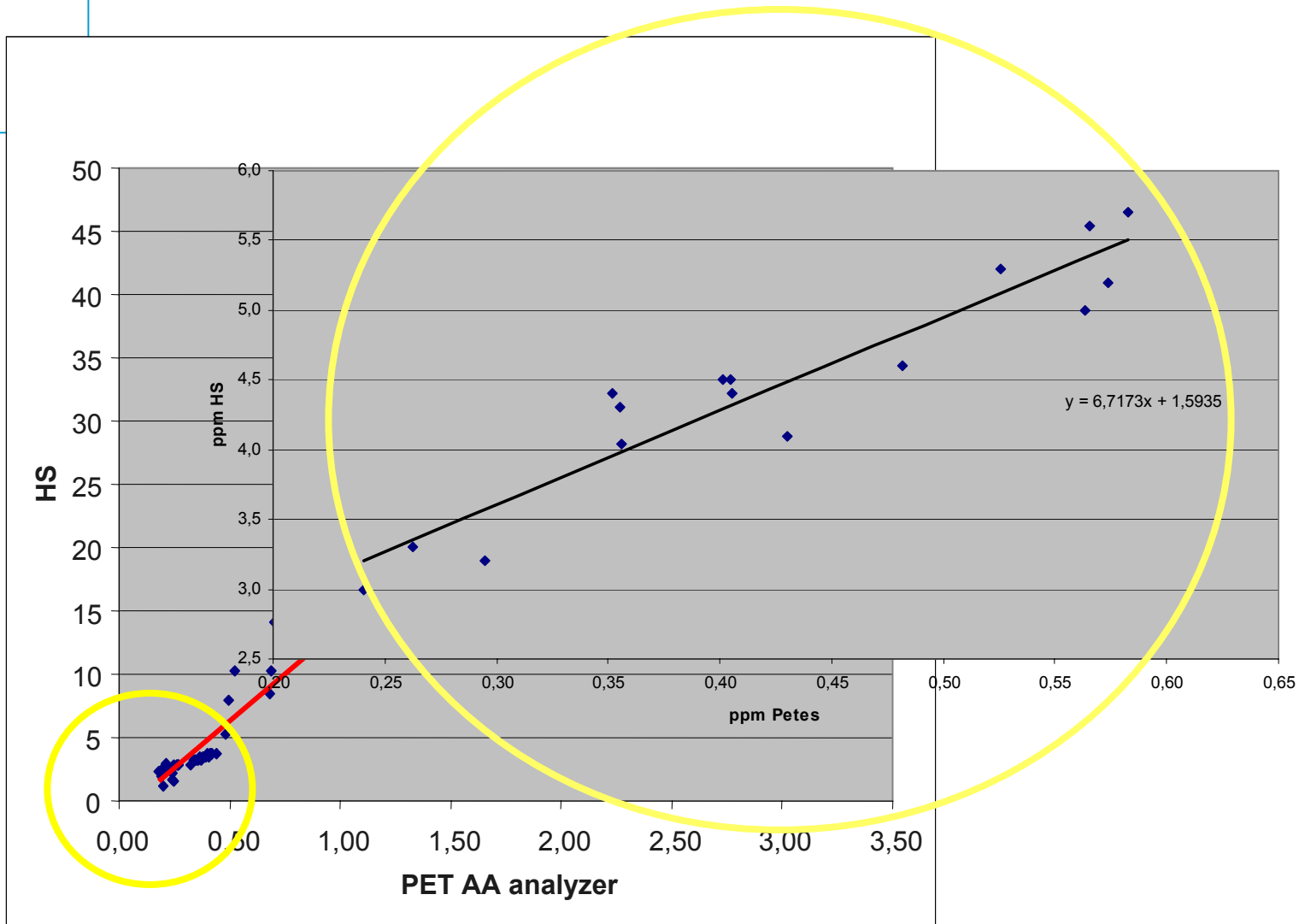


	<i>volume</i>	<i>area</i>	<i>ug AA</i>	<i>factor</i>	<i>ppm PET</i>	<i>test volume</i>	<i>Vtot/Vtest</i>	<i>real ppm</i>
empty	0	33809	7,5	4507,9		150,00	1,000	0,00
A	8577,52	164697	37,5	4140,8	36,42	141,42	1,061	34,34
B	7236,81	163043	37,5	4138,1	36,05	142,76	1,051	34,31
C	11576,97	167862	37,5	4130,8	37,12	138,42	1,084	34,26
D	12630,79	169971	37,5	4150,9	37,58	137,37	1,092	34,42
A+B	15814,33	164805	37,5	3931,5	36,44	134,19	1,118	32,60
C+D	24207,76	175297	37,5	3920,2	38,76	125,79	1,192	32,50
ABCD	40022,09	220447	37,5	4310,1	48,75	109,98	1,364	35,74





Correlation between Methods



Correlation between Methods

Example of calculation

preform	weight	area PETes Analyzer	correct volume	K volume	area calculated	real AA ug	PETes ppm	Trad. HS ppm	calculated K factor	delta methods	
1	16,50	26600	12,4	137,6	1,09	24408	5,9	0,36	4,0	4,0	0,0
2	16,32	42358	12,2	137,8	1,09	38906	9,4	0,57	5,2	5,4	0,2
3	16,43	32002	12,3	137,7	1,09	29376	7,1	0,43	4,1	4,5	0,4
4	16,47	41996	12,3	137,7	1,09	38542	9,3	0,56	5,0	5,3	0,3
5	16,47	30174	12,3	137,7	1,09	27692	6,7	0,40	4,5	4,3	-0,2
6	16,45	39135	12,3	137,7	1,09	35920	8,6	0,53	5,3	5,1	-0,2
7	19,20	25976	14,4	135,6	1,11	23485	5,7	0,29	3,2	3,6	0,4
8	19,12	35226	14,3	135,7	1,11	31863	7,7	0,40	4,5	4,3	-0,2
9	19,04	22918	14,3	135,7	1,11	20739	5,0	0,26	3,3	3,4	0,1
10	19,00	30663	14,2	135,8	1,10	27754	6,7	0,35	4,4	4,0	-0,4
11	19,35	21409	14,5	135,5	1,11	19340	4,7	0,24	3,0	3,3	0,3
12	19,10	31152	14,3	135,7	1,11	28181	6,8	0,36	4,3	4,0	-0,3
13	19,45	36282	14,6	135,4	1,11	32758	7,9	0,41	4,4	4,3	-0,1
14	19,20	49870	14,4	135,6	1,11	45088	10,9	0,57	5,6	5,3	-0,3
15	16,82	36764	12,6	137,4	1,09	33676	8,1	0,48	4,6	4,8	0,2
16	16,45	43352	12,3	137,7	1,09	39791	9,6	0,58	5,7	5,4	-0,3



Operation - Dedicated software

The screenshot displays the PETes AA Analyzer software interface. The main window features a central schematic of the instrument with various control panels and data readouts.

Control Panels:

- H2 FID (bar):** SET 3.5, NOW 3.4
- CARR. (bar):** SET 1.1, NOW 2.4
- AIR FID (bar):** SET 3.5, NOW 3.4
- AIR SERV.:** SET 3.5, NOW 3.4
- PRESS. (bar):** SET 1.1, NOW 2.4
- T.OVEN (°C):** SET 55, NOW 51
- T.DESORB. (°C):** SET 55, NOW 51

Data Readouts:

- VOLT: 9.999
- 43
- IGN R.: 0
- TC SIG: 4095
- 173, 10,

Function Keys:

- F1 HELP
- F2 PARAMETERS
- F3 CALIBRATION
- F4 ANALYSIS
- F5 TEST
- F6 FLAME IGNITION
- F7 PRINT
- F12 EXIT

Status and Time:

- WAIT END PRECONDITIONING
- GIO 08/08/2002
- 14:18:35

stand-by phase



Operation - Preform loading



Preparation phase



Operation - Dedicated software

PETes AAAnalyzer
□ □ ×

PREFORM	123456789012345	12345	Pref 33 gr BPF Clear	▼
MACHINERY	1234567890		Husky 01 - 48 cavity	
WEIGHT (gr)	33.0			
NECK	1234567890		BPF	
POLYMER	1234567890		Kosa T94	
COLOUR	1234567890		Clear	
ALARM AA (PPM)	3.0	METHOD	ASTM	
ALARM AA (PPB)	12.0	METHOD	HPLC 001-00	
MOULD	1234567890		48 cavity gen 1 #NOPQRSTUVWXYZABCDEFGHI	▼
CAVITY	1			
WORK ORDER N°	1234567890			
OPERATOR	1234567890		Ross Marion	▼
PRODUCTION DATE	07/08/2002	HOUR	22:35:00	

T.OVEN (°C)		AIR SERV.	
SET 55	NOW 51	SET 3.5	NOW 3.4
AIR FID (bar)		PRESS. (bar)	
SET 3.5	NOW 3.4	SET 1.1	NOW 2.4
CARR. (bar)		H2 FID (bar)	
SET 1.1	NOW 2.4	SET 3.5	NOW 3.4

STEP 1
SELECT PREFORM TYPE

STEP 2
INSERT PREFORM AND CLOSE

STEP 3
PRESS ENTER

F1 HELP

F2 ARCHIVES

F12 EXIT

AFTER CLOSING PRESS ENTER IMMEDIATELY

AVOID TO LEAVE PREFORM HEATING WITH CELL OPENED

ENTER

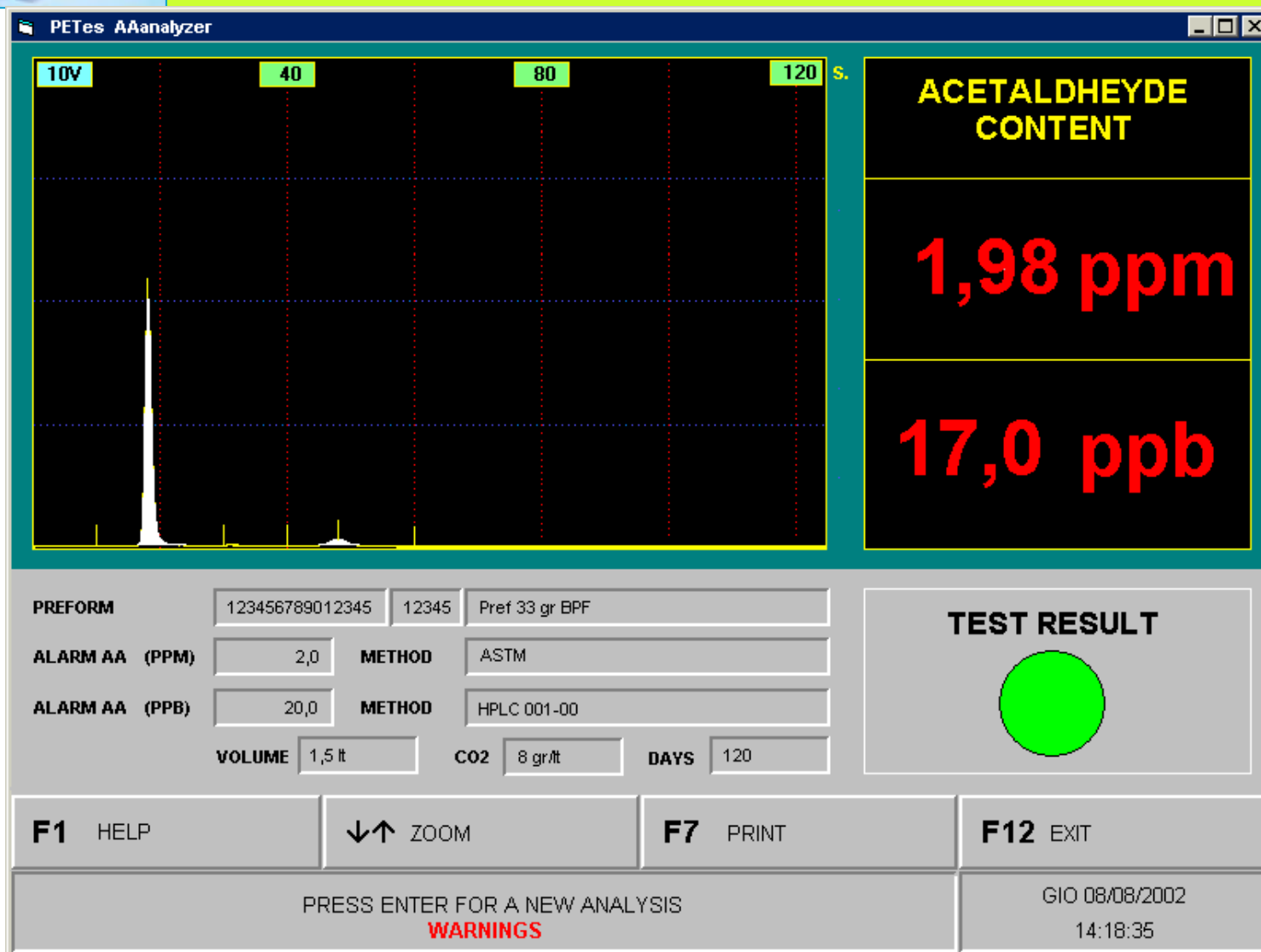
GIO 08/08/2002

14:18:35

Analysis phase



Operation - Dedicated software



Result





Printer and supply connections



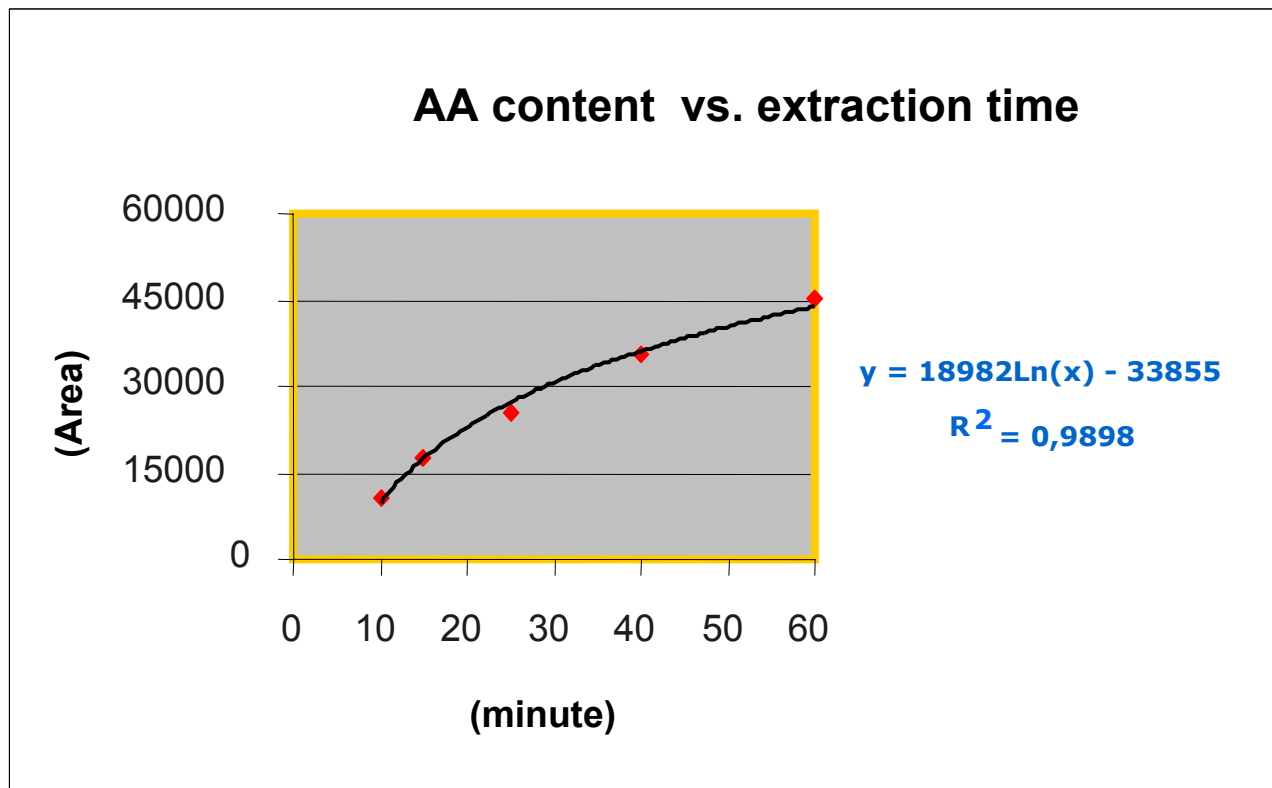
Advantages and Benefits

1. Reduction of the lag time in giving the AA results, increasing the process control
2. Simplification of the AA test
3. No skilled personnel
4. Location by the injection molding machine
5. Possibility of analysis on a wide range of preforms using the same de-adsorption cell
6. No sample preparation
7. Correlation with conventional test methods
8. Reliable results
9. No detection limit (below 0,5 ppm)
10. Highest repeatability
11. Automatic data elaboration
12. Cost Reduction of the AA test



Future innovation

Reduction of the analysis time



Offline and Online version




Online (process instrument)



Offline (lab instrument)



A photograph of several PET bottles on a tray. In the foreground, a large blue PET bottle is tilted. Behind it, a smaller green PET bottle is also tilted. In the background, another blue PET bottle is visible. The bottles are resting on a light-colored, possibly white, tray. The background is a solid light blue color.

PETes AA Analyser

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