

# **Chemical Reliability**



# Soldering Chemistry - general

# What does reliability of soldering chemistry mean?

• The residues and reaction products of the soldering process cannot influence the functionality of the electronic circuit.

# What can go wrong

- Drop of the Surface Insulation Resistance (SIR)
- Leakage currents
- Corrosion/Pickling (Removal of surface metal)
- Electro migration (metal atoms are dissolved and deposited somewhere else)

### Possible related causes

- Soldering Chemistry
- Residual chemistry from PCB- manufacturing
- Deposits from a polluted atmosphere
- Conductive or metallic residues or deposits from bad processing, handling or environment
- Water condensation



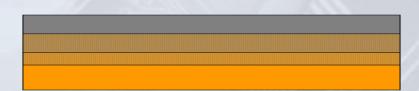


# Soldering Chemistry - general

• Main task of soldering chemistry is to clean (desoxydise) the surfaces of the metals to be joined.



• By cleaning the surfaces, the surface tensions are influenced in a way that a wetting of the solid metal by the liquid metal can take place.





# Soldering Chemistry - general

- The soldering chemistry is contained in a flux.
  - → Liquid flux: wave soldering flux, selective soldering flux, repair flux, tinning flux,...
  - → Gel flux: solder paste flux, solder wire flux, flux gels for repair
- Important components of a flux are
  - → Activators
  - → Rosin or resin
  - → Solvents
  - → Thixotropic agents (gel fluxes)
  - → Surfactants (Liquid fluxes)



# Soldering Chemistry – important components

The components of the flux that influence reliability the most are:

- Activators: → Perform the job of cleaning the metals
  - → Can create reaction products that are dangerous for reliability
  - → Can influence reliability in an unconsumed state
- Rosin or resin : → Determine many properties of the flux in the production process
  - tackiness
  - stability
  - dispensing capability
  - pin testability
  - cleanability
  - -...
  - → Encapsulate and protect the reaction products from the atmosphere (positive side effect but limited in time: ageing, cracking,...)



## Soldering Chemistry - Activators

Two main categories of activators exist

- Organic Acids
- a very large number of organic acids exist
- not every acid is suitable for electronics :
  - → solubility within the flux
  - → limited activity
  - → reliability
- reaction products <u>can</u> have low water solubility and <u>can</u> be very safe

СН3СООН

Example: Acetic acid is an organic acid



# Soldering Chemistry - Activators

- Halogens/ Halogenated activators
- contain either Cl, Br, F (I)
- very active
- have etching capability (react with metals)
- reaction products can have high water solubility and can be dangerous for reliability

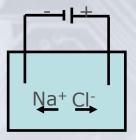
<u>H</u>		2															<u>He</u>
<u>Li</u>	<u>Be</u>											<u>B</u>	<u>C</u>	<u>N</u>	<u>O</u>	Ē	<u>Ne</u>
<u>Na</u>	Mg											<u>Al</u>	<u>Si</u>	<u>P</u>	<u>S</u>	<u>CI</u>	<u>Ar</u>
<u>K</u>	<u>Ca</u>	<u>Sc</u>	<u>Ti</u>	<u>V</u>	<u>Cr</u>	Mn	<u>Fe</u>	Co	<u>Ni</u>	Cu	<u>Zn</u>	<u>Ga</u>	<u>Ge</u>	<u>As</u>	<u>Se</u>	<u>Br</u>	<u>Kr</u>
<u>Rb</u>	<u>Sr</u>	<u>Y</u>	<u>Zr</u>	<u>Nb</u>	<u>Mo</u>	<u>Tc</u>	Ru	<u>Rh</u>	<u>Pd</u>	<u>Ag</u>	<u>Cd</u>	<u>In</u>	<u>Sn</u>	<u>Sb</u>	<u>Te</u>	Ţ	<u>Xe</u>
<u>Cs</u>	<u>Ba</u>	*	<u>Hf</u>	<u>Ta</u>	<u>W</u>	<u>Re</u>	<u>Os</u>	<u>lr</u>	<u>Pt</u>	<u>Au</u>	<u>Hg</u>	<u>TI</u>	<u>Pb</u>	<u>Bi</u>	<u>Po</u>	At	<u>Rn</u>
<u>Fr</u>	<u>Ra</u>	**	<u>Rf</u>	<u>Db</u>	<u>Sg</u>	<u>Bh</u>	<u>Hs</u>	Mt	<u>Ds</u>	<u>Rg</u>	<u>Uub</u>	<u>Uut</u>	<u>Uuq</u>	<u>Uup</u>	<u>Uuh</u>	<u>Uus</u>	<u>Uuo</u>



### **Soldering Chemistry - Water solubility**

- The water solubility of the reaction products or the soldering chemistry can have a large influence on the reliability
- Reaction products with organic acids, when designed well, usually have very low water solubility
- Reaction products with halogens usually have very high water solubility
- → The product dissolves in a watery environment into ions
- ightarrow Under electrical voltage the ions will function as transport of electrons: electrical leakage current, reduction of SIR

Example: NaCl (Kitchen salt) +H2O → Na+ + Cl-



→ Under circumstances electro migration can happen. Atoms are dissolved and deposited elsewhere





# **Soldering Chemistry - Water solubility**

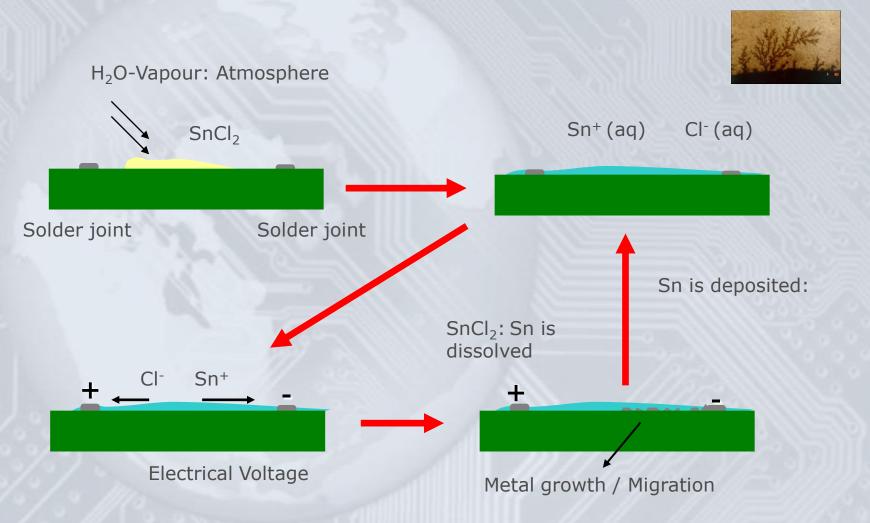
		Solubility in
	Chemical	cold water
Metal salt	designation	(g/100cc)
Lead chloride	PbCl <sub>2</sub>	0,99
Copper chloride	CuCl <sub>2</sub>	70,6
Silver chloride	AgCl	89x10 <sup>-6</sup>
Tin chloride	SnCl <sub>2</sub>	83,9

Water solubility of some halogenated metal salts

- Metal salt with Sn has the highest water solubility
- Lead-free alloys, can contain up to 99,3% of Sn in case of SnCu0,7, 96,5% for SAC305



# Soldering Chemistry: electro migration



# Soldering Chemistry - Rosins and Resins

- Rosin
- natural product
- limited heat resistance: discoloration, embrittlement
- good tackiness
- heavy residues : pin testing contact problems
- fumes can be harmful (hand soldering)
- chemical modification of the rosin can influence most of these properties



- synthetic product
- better heat resistance: less discoloration
- in general less tackiness
- in general less heavy residues
- fumes are less harmful
- huge variety of different types







#### PCB technology in the past

- Base materials with low insulation resistance and high moisture sensitivity
- Single sided boards for wave soldering
- Large distances between the Cu-tracks and the components
- Limited solderability of board and components
- Wave soldering machine technology was limited



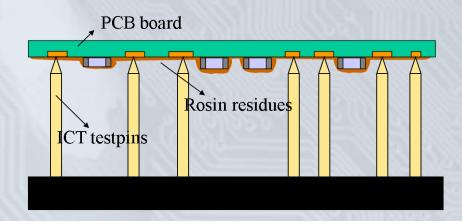
- → Liquid flux technology was highly activated with halogens
- → For reliability high rosin contents were used in the flux (>30%)



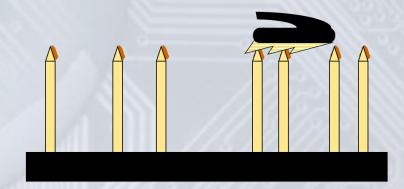


Problems with the high rosin content

• ICT contact problems : bottleneck in the production flow



• High test pin usage due to cleaning : high cost

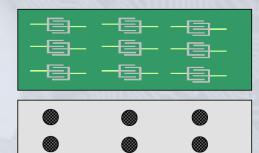


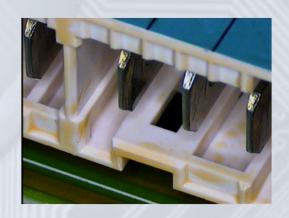


Problems with the high rosin content

• contact problems on push buttons (e.g. remote control)

contact problems in connectors







Problems with the high rosin content

- Blocking of fluxing units : process instability
- High machine pollution and maintenance
- High carrier pollution and maintenance





#### Evolutions in PCB technology



base materials with higher insulation resistance and lower moisture sensitivity



double sided boards / multilayer



• smaller distances between the Cu-tracks and the components



• SMD technology ( mix of different kinds of soldering chemistry)



better solderability of board and components



more sophisticated machine technology



#### → flux technology gradually reduced its activation levels

- reduction of the amount of halogens
- introduction of organic acids
- introduction of absolutely halogen free flux formulations
- → rosin contents were also gradually reduced
  - introduction of resins
  - introduction of No-residue<sup>™</sup> technology (Interflux® patent)



Introduction of new soldering technologies

- Selective soldering
- turbulent wave wash off the flux more rapidly
- higher temperatures are used
- not the total area that has been sprayed with flux passes through the soldering process
- Selective soldering carriers
- cover parts of the board that cannot pass through the wave (e.g. reflowed components)



- flux will penetrate between the carrier and the board and will not see the wave
- Carrier will shield the heat transfer to the board, more heat needs to be applied to preheat the board, non covered parts will see much more heat
- $\rightarrow$  Tendency to use fluxes with more activation
- $\rightarrow$  theoretically contradictory to the unconsumed flux chemistry in these processes



#### June 2006 RoHS

- RoHS compliant base materials have higher moisture sensitivity
- Higher process temperatures
- Current lead-free alloys have: higher oxidation levels

lower solder spreading behaviour

higher melting points

- → Tendency to increase the activity of soldering chemistry
- → IPC allows the usage of 500ppm of halogens for the lowest activation class "L0"
- → Halogenated metal salts have high water solubility especially when containing Sn



→ Contradictory



### **Soldering Chemistry - Summary**

Important parameters in reliability of soldering chemistry are:

- Water solubility of the reaction products
- Behaviour of the chemistry in an unconsumed state
- Protection capacity of the body (Rosin/ Resin,...)
- Fatigue properties of the body (ON/OFF Frequency, thermal cycling, ageing,...)
- → Most of these Parameters can be controlled in the development of the soldering chemistry where:
- The design of the activator package is the most crucial step in development
- The choice of rosin or resin can "cover up" for critical activators, but limited in time
- Atmospheric Conditions: Temperature, Moisture
- → This parameter cannot be controlled in development of soldering chemistry
- → It is simulated in reliability testing



# Reliability testing - general

- Their main purpose is to test the reliability of the soldering chemistry after soldering
- The result of the test can indicate whether the residues of the soldering chemistry can remain on the board : No-clean flux (solder paste, solder wire)
- Many different kinds of reliability tests exist
- Most electronic manufacturers still refer to IPC: an American standardisation organisation
- Others: European standard: EN

Japanese standard: JIS

German standard: DIN

Telecom standard: Bellcore

- Many OEMs have their own reliability tests: Automotive, Siemens, Schneider, HP,...
- Main concern lately: Do reliability tests give a realistic simulation of the processes in manufacturing and the conditions that the board experiences in the field
- $\rightarrow$  More and more reports of field failures caused by soldering chemistry that passes reliability tests

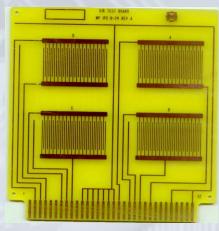


# Reliability testing - Surface Insulation Resistance test (SIR)

#### IPC J-STD-004B

Flux is being applied to a special comb pattern (0,4mm width, 0,5mm distance) and it is being soldered with dedicated parameters. The surface insulation resistance is being measured during 7 days, at least once every 20min, at 40 C, 90% R.H. and 5VDC.

- → Surface insulation resistance cannot drop below 100 MOhm.
- → Visual inspektion on dendrites, corrosion, anomalies,...



IPC-B-24



### Reliability testing - Migration test

#### **Migrationstest: IPC J-STD-004B**

Flux is being applied on a special comb pattern (0,318mm Breite und 0,318mm) and it is being soldered with dedicated parameters.

The SIR is being measured after 96hrs of stabilisation and after 596 hrs with 45VDC to 100VDC. Test voltage is 10 VDC at at 40 C and 93%RF or at 65 C and 88,5%RF or at 85 C and 88,5%RF 5 VDC

- → SIR cannot drop more than 1 decade
- ightarrow Visual inspection on migration and anomalies with 10X scope

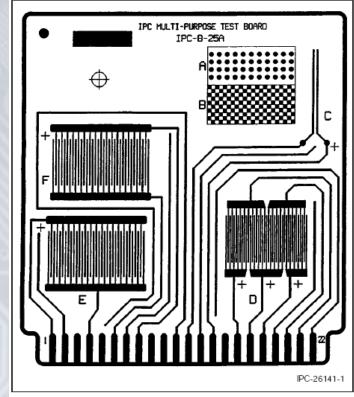


Figure 1 IPC-B-25A Test Board



# Reliability testing – other examples

Standard	SIEMENS SIR	SIEMENS ECM	IPC-J-STD 004B SIR	IPC-J-STD 004A SIR	Bellcore SIR	Bellcore ECM	
Temperature/ Humidity	40 C/ 93%RH	40 C/ 93%RH	40 C/ 90%RH	85 C/ 85%RH	35 C/ 85%RH	65 C/ 85%RH	
Test duration	168hrs	168hrs	168 hrs	168hrs	96 Hours	500 Hours	
Measurement frequency	, , , , , , , , , , , , , , , , , , , ,		Continuous monitoring	At 24hrs, 96hrs and 168hrs	Measured at 24 hrs, 96 hrs	Measured at 500 hrs	
Measuring Bias			5V 5V	100V -50V	100V -50 V	100V 10 V	
Test Coupon			IPC-B-24	IPC-B-24	IPC-B-25A	IPC-B-25A	
Gap track	0.2mm 0.4mm	0.2mm 0.4mm	0.5mm 0.4mm	0.5mm 0.4mm	0.32mm 0.32mm	0.32mm 0.32mm	
Conditions	100 C / 100 C / 5min.  No solder  wave pass through  100 C / 5min.  No solder  wave pass through		Pattern up/down Solder wave	Pattern up/down Solder wave	Pattern up/down Solder wave	Pattern up/down Solder wave	
Minimum Resistance values	Resistance ≥1.5x100M der		Not cleaned ≥100MΩ	Not cleaned ≥100MΩ	2x10 <sup>4</sup> MΩ	Not cleaned < 1 decade drop	



### Reliability testing - remarks

#### Remarks

- Most test do not count with a situation of unconsumed flux chemistry
  - selective soldering
  - selective wave soldering carriers

#### Solution: Run a fluxed but a non processed board with the tests

- Most tests do not count with ageing of rosin or resin residues
  - They can lose their protective capacity in the field due to thermal cycles.
     When heating up and cooling down due to the functioning or environment,
     the residue is expanding and retracting together with the board. Cracks can appear and the protective capacity has been lost.

Solution: Run thermo cycles prior to testing

Problem: Risk of water condensation on the board



# Reliability testing - remarks

• Bias Voltage of 50 VDC is quite high, electro migration can theoretically happen without being noticed. When electro migration happens, it grows quite fast at this voltage, when it creates a short, it can be burned away.

#### 5 VDC is better

•Measuring at 24,96 and 168 hrs gives the risk that temporary drops and recoveries in insulation resistance are not measured.

Solution: Measure "continuously"



### Reliability testing - Test Bono

• Purpose of the test is to create a very sensitive situation where the interaction of all fluxes can be measured. It uses a very fine Cu structure from a built up process. The test is designed that if the test would continue, all fluxes and solder pastes would fail in the end.





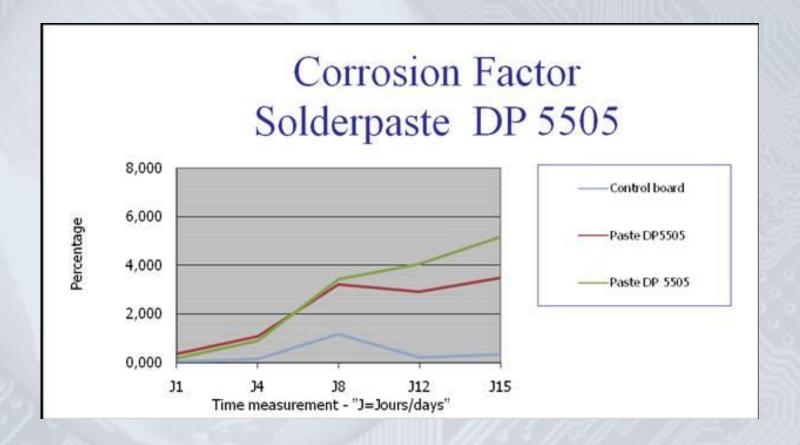
# Reliability testing - Test Bono

- In between to wide cathodes, there is a very fine anode of 9µm by 75µm. The resistance of the track is about 3w.
- liquid flux
  - thin layer of flux is applied
  - pattern is soldered pattern up

- gel flux ( or solder paste)
  - gel flux is printed on the cathodes
  - reflow profile
  - residues must flow out over the anode
- One untreated control board runs with the processed boards
- After 2 hours at 25 C and 50% R.H. the atmosphere is changed to 85 C and 85% R.H.
- After 16hrs of stabilisation, the initial resistances (Ro) of the anodes are measured
- a Bias Voltage of 20VDC is applied for 15 days
- The resistances of the anodes (Rj) are measured with 11V DC at 24, 96, 168, 288 and 360 hrs
- A corrosion factor is calculated: F<sub>c</sub> (Rj-Ro)/Rox100
- The corrosion factor cannot be more than 8%



# Test Bono





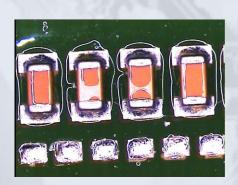
# Reliability testing - Summary

- If a unit is being soldered with a soldering chemistry that passes a certain reliability test, it is no guarantee that the board will have no reliability problems in the field.
- A lot of parameters come together and most reliability tests do not cover all these parameters.
- Some electronics are more sensitive towards leakage currents than others (high resistance circuits, high frequency circuits,...)
- The conditions where a unit is submitted to in the field can be very different: Polluted atmosphere, Temperature changes, water condensation...
- It can be useful to perform a reliability test designed by yourself on a critical unit. This test should be performed on the unit itself. The conditions where the board is submitted to in the field should be simulated and accelarated as good as possible.



# Soldering chemistry and conformal coating

- Most manufacturers do not clean before applying a conformal coating.
- In most cases, a general adhesion is obtained. The quality of the adhesion can be tested according e.g. IPC CC 830









Scratch test



# Soldering chemistry and conformal coating

• The adhesion after thermal cycling is very often problematic, but is rarely tested.



Big cracks in the coating after 1000 cycles -40 C/+125 C



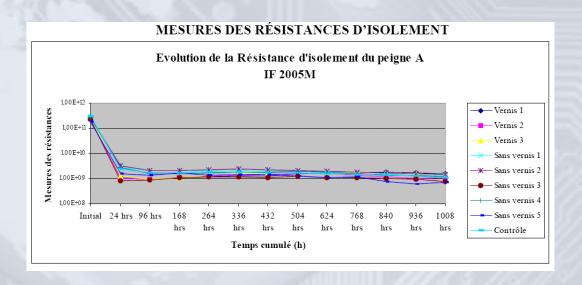
Detaching of the coating after 250 cycles -40 C/+125 C

- The soldering chemistry and the compatibility with the coating are crucial in this matter.
- No-residue<sup>™</sup> chemistry has very high compatibility with all coatings.



# Soldering chemistry and conformal coating

- Some manufacturers perform a migrationtest after thermal cycling of the board. This gives a much better picture of the compatibility between coating and soldering chemistry.
- Example: 1000 Cycles -55 C / +125 C
  - 1000 hrs at 85 C 85% RH at 50VDC

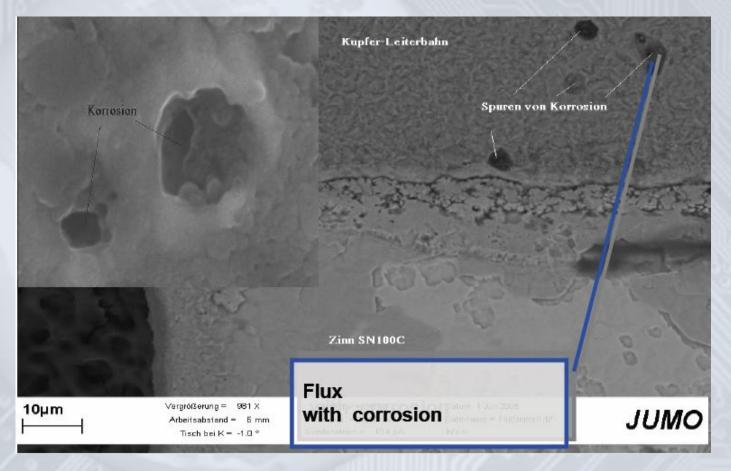




- Automotive application that had problems with corrosion after switching over to lead-free alloys while the soldering chemistry remained the same
- Automotive Class 1 ( IPC Class 3 = highest class)
- Cu selectively soldered with SnCuNi
- Application very sensible for Cu-Corrosion
- 5 VDC
- 2000 Cycles 0-150 C (1 Hr/ Cycle)
- An electron microscope is used for detecting corrosion.

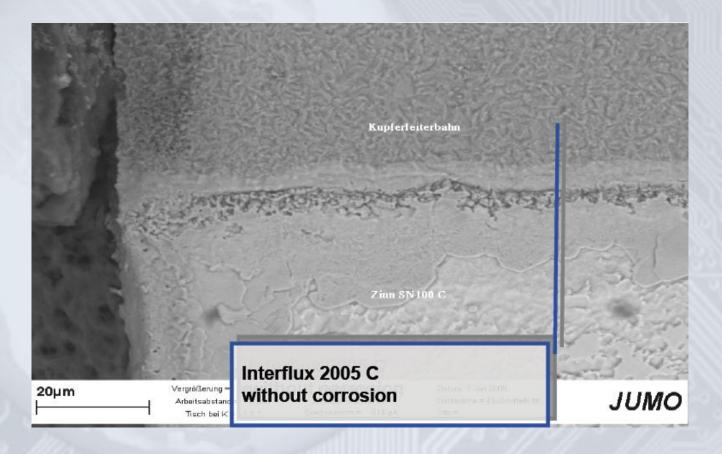


• flux used for SnPb but giving corrosion when changing over to lead-free alloys



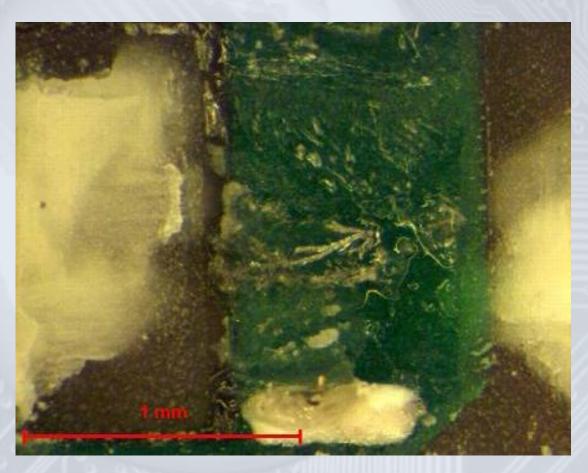


#### Absolutely halogen free soldering flux solved the problem





• Dendritic growth underneath a ceramic capacitor causing a failure in the field

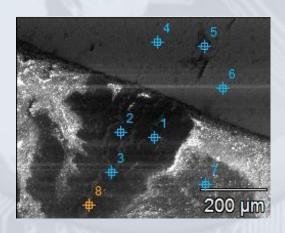


- •Cl was found
- •L1 solder paste



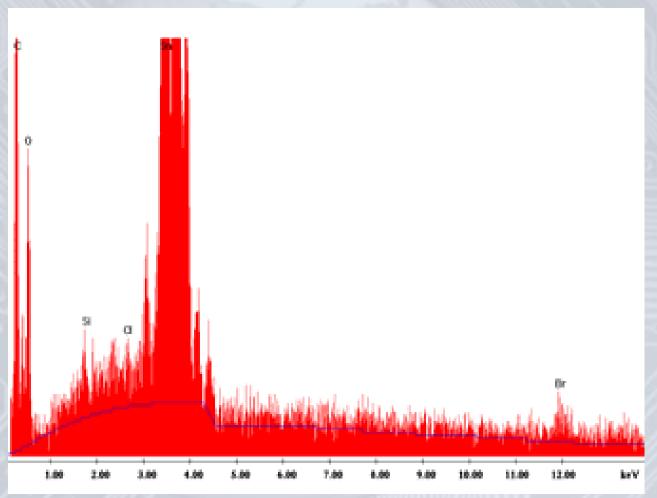
# S.E.M analysis

- Scanning electron microscope
- → high-energy beam of electrons is applied to a surface. The reaction signals (electromagnetic radiation, backscattered electrons,...) are analysed
- → can be used for element analysis
- → can be applied to a very small surface
- → very good indication method for reliability problem analysis
- → sensitive to calibration of the machine
- → Differences in accuracy from machine to machine





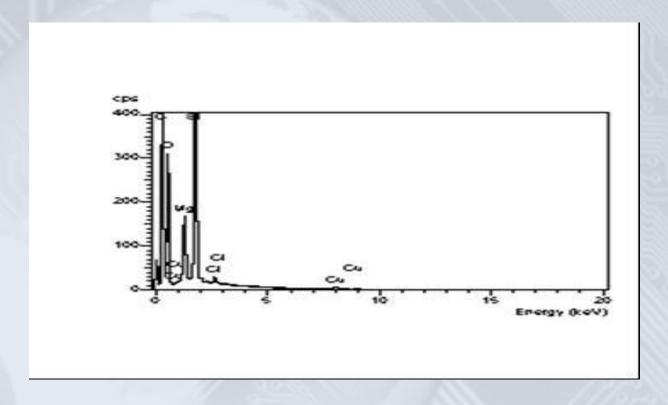




- Detection of Cl and Br
- Soldering chemistry



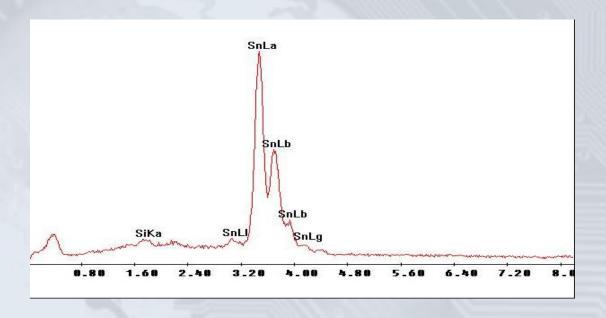
# Examples of S.E.M analysis of field reliability problems



- Analysis on electro migration found on PCB
- Cl : soldering chemistry ?



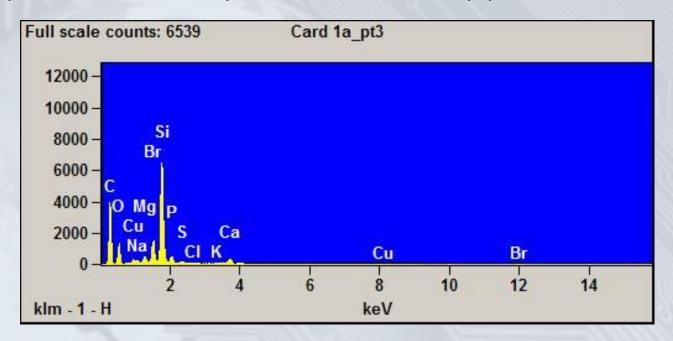
# Examples of S.E.M analysis of field reliability problems



- White traces found on solder mask after wave soldering
- Sn: Sn adhering to badly cured or bad solder mask?
  - Bad wave settings ,bad backflow ?
  - Heavily oxidized solder in solder pot?
- Si : Typical element of solder mask



# Examples of S.E.M analysis of field reliability problems



- Analysis on black trace found on the solder mask
- Cl : Soldering chemistry ?
  - NaCl: salt from handling, sweat,...?
  - Tab water? → CaCo<sub>3</sub>, Mg, Na, K,...
- Br: Soldering chemistry ?
  - Flame retardant ?

- S: Residual PCB manufacturing chemistry?
  - Polluted atmosphere ?

