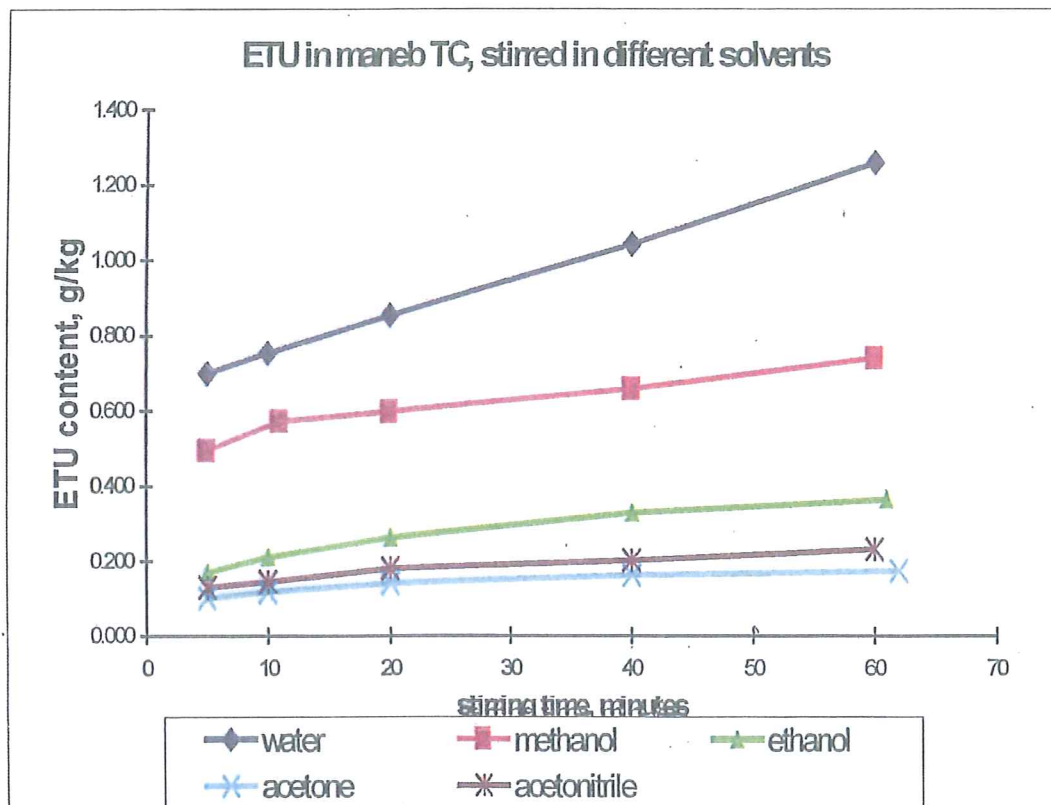


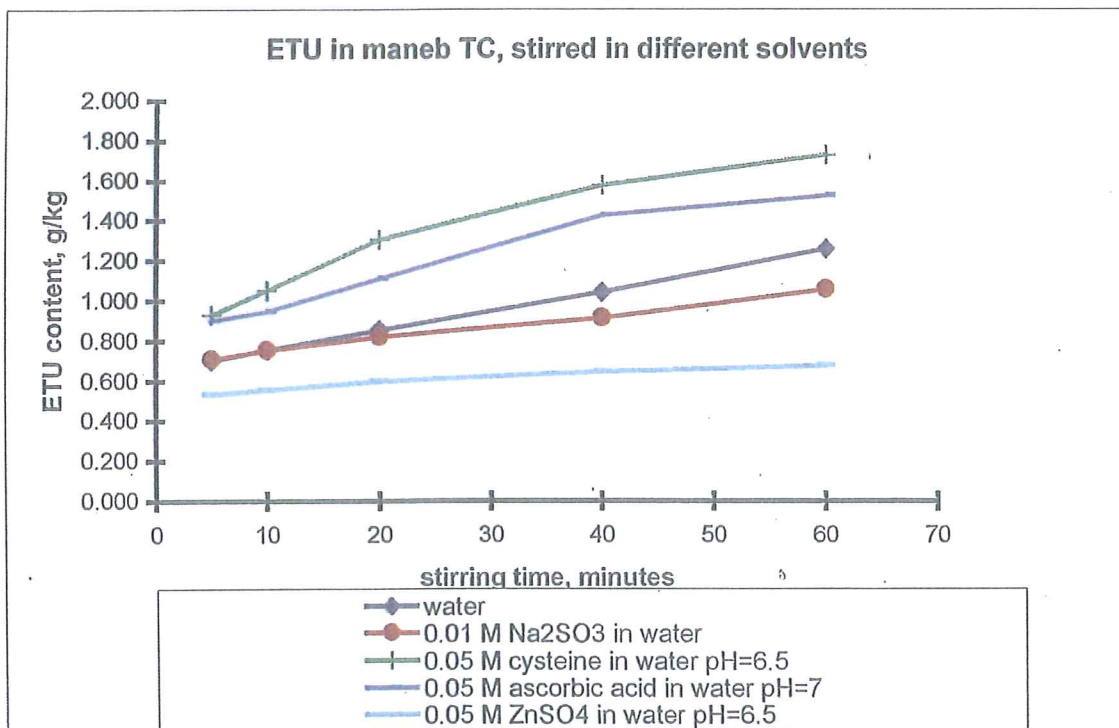
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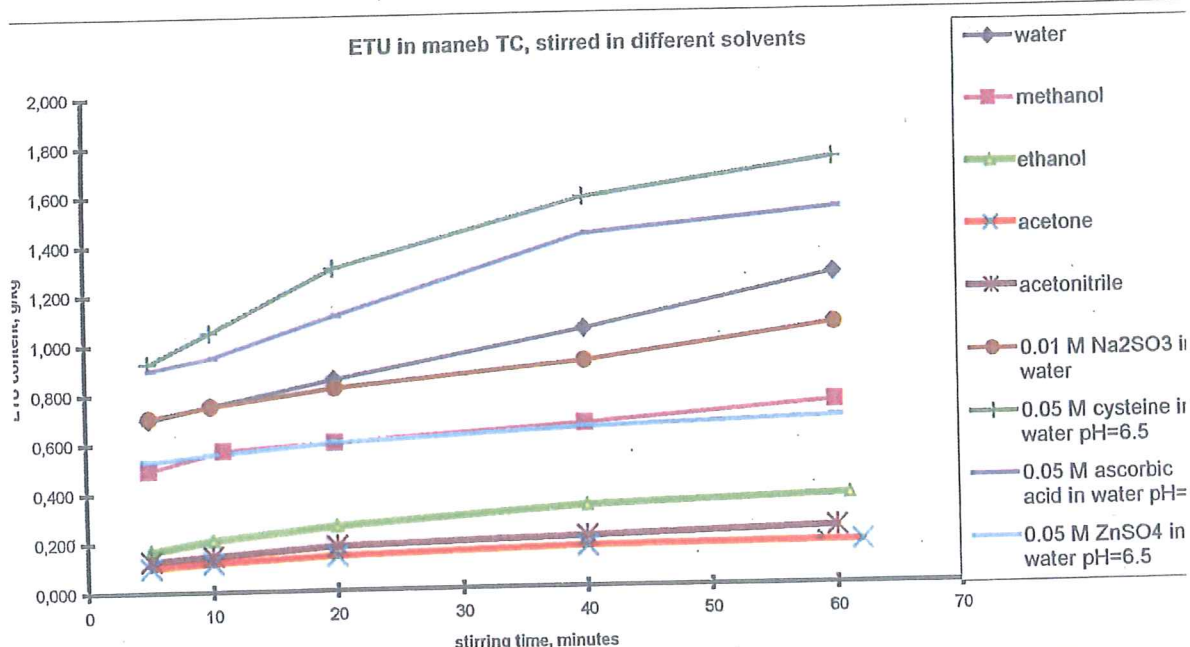


**Water containing reducing agents, stabilisers and solubility suppresser**





### COMBINED GRAPHS



1. In all solvents increasing ETU content with increasing extraction times
2. All different solvents seem to have different in situ ETU concentrations
3. The increase rate in the solvents is different
4. Solubility of EBDC is a disturbing factor. See difference between water and ZnSO<sub>4</sub> solution
5. Prevention of oxidation plays a role. See difference between water and sulphite solution

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**We are interested in :**

- **Initial ETU content**
- **Most stable solution**
- **Does the solubility of ETU in the solvent play a role**
- **Does the solubility of maneb play a role in the different solvents**
- **Is the difference in ETU content between the different solvents due to decomposition or extraction efficiency**



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Regression data on observed ETU content vs. stirring time  
2<sup>nd</sup> order polynomial

Solvent	parameters			correlation coefficient
	x <sup>2</sup>	x	intercept	
water	1*10 <sup>-5</sup>	0.0094	0.66	0.9998
methanol	-3*10 <sup>-5</sup>	0.0059	0.49	0.981
ethanol	-6*10 <sup>-5</sup>	0.0071	0.14	0.998
acetone	-3*10 <sup>-5</sup>	0.0029	0.09	0.996
acetonitrile	-2*10 <sup>-5</sup>	0.0032	0.12	0.989
0.01 M Na <sub>2</sub> SO <sub>3</sub> in water	4*10 <sup>-6</sup>	0.0059	0.69	0.996
0.05 M cysteine in water pH=6.5	-2*10 <sup>-4</sup>	0.0290	0.79	0.9993
0.05 M ascorbic acid in water pH=7	1*10 <sup>-4</sup>	0.0215	0.77	0.9948
0.05 M Zn SO <sub>4</sub> in water pH=6.5	-4*10 <sup>-5</sup>	0.0049	0.51	0.9986



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**Solubility of ETU in 5 minutes stirring in the investigated solvents**

<b>solvent</b>	<b>ETU in solvent (mg/ml)</b>	<b>Expressed as ETU g/kg maneb</b>
<b>water</b>	<b>21.9</b>	<b>438</b>
<b>ethanol</b>	<b>6.9</b>	<b>139</b>
<b>methanol</b>	<b>17.4</b>	<b>349</b>
<b>acetone</b>	<b>9.6</b>	<b>191</b>
<b>acetonitrile</b>	<b>9.9</b>	<b>198</b>

The solubility of ETU in all investigated solvents is adequate to cope with the expected ETU contents in EBDC.

**Recovery of ETU at 10 g/kg level**

<b>solvent</b>	<b>dissolved ETU (%)</b>
<b>water</b>	<b>103</b>
<b>ethanol</b>	<b>102</b>
<b>methanol</b>	<b>102</b>
<b>acetone</b>	<b>102</b>
<b>acetonitrile</b>	<b>102</b>

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### Dissolution of maneb

<b>solvent</b>	<b>dissolved maneb (mg/l)</b>
<b>water</b>	<b>176</b>
<b>ethanol</b>	<b>1</b>
<b>methanol</b>	<b>4</b>
<b>acetone</b>	<b>&lt;1</b>
<b>acetonitrile</b>	<b>6</b>
<b>ZnSO4 sol</b>	<b>2</b>

In water the maneb is dissolved: obviously the dissolved maneb plays a role in the ETU formation. In methanol and ethanol other reactions are involved.

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How do other decomposition products of EBDC behave in these solvents ?

In EBDC's always small amounts of sulphur and DIDT (5,6-dihydro-3H-imidazo[2,1,c]-1,2,4-dithiazole-3-thione) are found.

The latter is also called EBIS (ethylenebis(isothiocyanate)sulphide) and is reported to be the most fungicidally active component.

DIDT and Sulphur found after 5 min extraction

solvent	DIDT (g/kg)	sulphur (g/kg)
water	1.15	0.58
methanol	2.14	1.40
ethanol	0.84	0.59
acetone	0.43	0.49
acetonitrile	0.55	0.52

In water and methanol the highest concentration of other decomposition products is found.



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**DIDT and Sulphur found in maneb and solubilities in solvents**

solvent	found in maneb		dissolved in 1 hr	
	DIDT (g/kg)	sulphur (g/kg)	DIDT (g/kg)	sulphur (g/kg)
water	1.15	0.58	3.0	0.0
methanol	2.14	1.40	107	4.9
ethanol	0.84	0.59	n.a	n.a
acetone	0.43	0.49	163	12.0
acetonitrile	0.55	0.52	239	4.0

**Conclusions:**

The amounts of DIDT found are the highest in the solvents with the lowest dissolution capability

The amount of sulphur found in maneb is the highest in methanol and not in acetone which is a better solvent for sulphur.

In the water extract of maneb sulphur is found, while in water elemental sulphur will not dissolve. The sulphur is formed, in statu nascendi

**THESE OBSERVATIONS EMPHASISE THE THESIS THAT DECOMPOSITION TAKES PLACE!**

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As next to ETU, DIDT and Sulphur are metabolites of Maneb and are found in the highest concentration in methanol and water it emphasizes the thesis of Clarke et al. that these compounds are generated during extraction.

These compounds can only arise from the degradation of maneb!