International Chemistry Olympiad 1998: Three Medals for Switzerland

Switzerland has made a remarkable string of successes in the 30th International Chemistry Olympiad 1998 with three bronze medals. Only once in the past years had we obtained such a high number of medals, and it was in 1990 in Pittsburgh, USA.

This competition took place from July 5–13, 1998 in Melbourne, Australia. Forty-eight countries sent their best four students from the secondary level. After theoretical and practical examinations both lasting five hours, the best students were rewarded by gold, silver, and bronze medals. The first 10% got gold medals, 20% got silver, and 30% bronze.

The theoretical tasks are given with full details in annex, with their solutions. Try to solve them in less than five hours, as did our Swiss candidates!

The best results went to a Chinese student (95 points out of a maximum of 100 points), before an American. As a whole, the best nation was Hungary with 3 gold medallists, before Argentina, Germany, Korea, Singapore, United Kingdom, and USA, each having two gold medals.

National teams are usually formed of four students and two mentors. The four Swiss competitors were selected at Easter 1997 at the Gymnase de Chamblandes, Pully, Lausanne, at the end of a training week. They are:
- *Luca Castiglioni*, 6313 Menzingen ZG, born 25.1.1979, Bronze
- *Dominik Langer*, 8912 Obfelden ZH, born 12.12.1978, Bronze
- *Massimo Lurati*, 6952 Canobbio TI, born 2.10.1979, Bronze
- *Stefan Ottiger*, 8910 Affoltern ZH, born 26.9.1978.

Luca Castiglioni and *Stefan Ottiger* were both from the Kantonsschule Zug,

Dominik Langer from the Kantonsschule Limmattal, and *Massimo Lurati* from the Liceo di Lugano II.

The mentors were Dr. *Maurice Cosandey*, Pully VD, Dr. *Jochen Müller*, Zürich, and a young newcomer, the talented Dr. *Thomas Engeloch* from Reinach BL. The flights from Kloten to Melbourne were kindly offered by the New Swiss Chemical Society (NSCS) for the candidates and by the Bundesamt für Bildung und Wissenschaft for the teachers.

The next Chemistry Olympiads will happen in Bangkok 1999, Copenhagen 2000, and Hradec Kralove, Czechia, 2001. Switzerland makes plans for hosting an Olympiad in 2004. A dynamic committee has recently been formed in the NSCS for boosting this idea in our country under the leadership of Prof. *Reinhard Neier*.

Maurice Cosandey

Theoretical Problem 1

Analysis of an alloy containing Pb and Sn.
1) A 0.4062-g sample of alloy is dissolved with an excess of mixture of 11M hydrochloric acid and 16M nitric acid. In this procedure, lead is oxidized to Pb^{II} and tin to Sn^{IV}.
2) After 5 min of heating to expel chlorine and oxides of nitrogen, the soln. is cooled and a precipitate appears.

Maurice Cosandey, Jochen Müller, the guide Malcolm, Stefan Ottiger, Massimo Lurati (bronze), Thomas Engeloch, Luca Castiglioni (bronze), Dominik Langer (bronze) (from left to right)

3) A 25.00-ml aliquot of a 0.2000M Na_2H_2EDTA soln. is added. The precipitate dissolves and a clear, colorless solution is obtained.

4) The soln. is quantitatively transferred to a 250.0-ml flask and made up to the mark with water.

5) A 25.00-ml aliquot of this soln. is treated with 15 ml of a 30% w/v solution of hexamine (hexamethylenetetramine), 130 ml of water, and two drops of xylenol-orange (XO) soln. The pH of the soln. is 6.

6) The clear, yellow soln. from step 5 is titrated with standard 0.009970M lead-nitrate soln. until the color just changes from yellow to red. Endpoint at 24.05 ml.

7) 2.0 g of solid NaF was added to the titration flask. The soln. immediately turns back to yellow.

8) The soln. was titrated with more 0.00970M lead nitrate until the color changes to red again. Endpoint 15.00 ml.

Questions:

1-1. What is the lead compound that precipitated in step 2?

1-2. Write a balanced equation that explains the disappearance of the precipitate in step 3.

1-3. What is the purpose of hexamine in step 5?

1-4. What is the purpose of xylenol orange in the analysis?

1-5. Write the equations for the reactions that occur *i)* during the titration and *ii)* when the color changes at the endpoint in step 6.

1-6. What is the purpose of NaF in step 7?

1-7. Write the corresponding equation for step 7.

1-8. Explain why the color changes from red to yellow in step 7.

1-9. Calculate the percentage by mass of Sn and Pb in the alloy.

Theoretical Problem 2
2.A. Dating Historical Events Using Pb-210

By drilling the sediments in the bottom of an Australian lake in 1995, European oak pollen was found down to a depth of 50 cm. The activity due to Pb-210 in this sediment was 356 Bq/kg at the surface and 1.40 Bq/kg at 50 cm depth. Pb-210 is one of the daughters of U-238 in the following decay scheme: U-238 – U-234 – Th-230 – Ra-226 – Rn-222 – Po-218 – Bi-214 – Pb-210 – Pb-206 (stable).

2-1. In what year did the first European tree appear in Australia?

2-2. Which step in the decay scheme explains how Pb-210 ends up in rain water while its parent U-238 is only present in the earth's crust?

2.B. Separation of Radionuclides

Ga-67 is produced by bombarding a target enriched in Zn-68 (98%) with high-energy protons for 11 h. Zn-68 has a natural abundance of 18.8%. The bombardment produces also the following radionuclides, with corresponding half-lives: Co-55 (18.2 h), Ni-57 (36.0 h), Co-57 (daughter of Ni-57, 270 d), Cu-64 (12.7 h), Cu-67 (61.7 h), Zn-65 (244 d), Ga-67 (78.35 h), Ga-66 (9.4 h). 12 h after the end of bombardment, Ga-67 is bound on a cation-exchange resin. The other radionuclides and Zn-68 are eluted in the wash soln. leaving Ga-67 bound to the column. The wash soln. is evaporated to dryness and the residue dissolved in a small amount of 0.2M HCl in 96% methanol and loaded into an anion-exchange column.

2-3. Use the following *D* values and choose the best solvent systems for eluting Co-55 and Cu-64.

The distribution coefficient is a measure of the partition of a metal ion between the ion-exchange resin and the eluant. It is defined by:

$$D = \frac{\text{radioactivity per mg of resin}}{\text{radioactivity per ml of eluant}}$$

For a reasonable separation of two metal ions, their *D* values should differ by at least 10 units.

Here are some numerical *D* values in an anion-exchange resin. For HCl in 96% methanol, $D > 1000$ for Zn, $D = 100$ for Cu^{II}, $D = 40$ for Co^{II}, $D = 0$ for Ni^{II}.

For 1M HCl in 55% propan-2-ol, $D = 1$ for Co^{II}, $D = 7$ for Cu^{II}.

For 2M HCl in 55% propan-2-ol, $D = 2$ for Co^{II}, $D = 30$ for Cu^{II}.

2-4. Having isolated relevant radionuclides, the presence of long-lived radionuclides could interfere with medical use of Cu-64, Co-55, or Ga-67. Indicate whether each of the following statements is true or false.

a) Ni-57 may be a contaminant of Co-55.

b) Co-57 will interfere with the medical use of Co-55.

c) Cu-67 will interfere with the medical use of Cu-64.

d) Ga-66 will interfere with the medical use of Ga-67.

e) Ga-67 will interfere with the medical use of Cu-64.

2-5. If radionuclide contamination of Cu-64 or Co-55 or Ga-67 occured, which method would reduce the amount of radionuclide contaminants? Indicate whether each of the following statements is true or false.

a) Remove Ni-57 before isolating Co-55.

b) Separate Ni-57 from the bombarded target material before isolating Ga-67.

c) Separate the radionuclides closer to the end of bombardment.

d) Allow Ni-57 to decay before isolation of Co-55.

2-6. If zinc of natural isotopic abundance, instead of enriched Zn-68, was bombarded with protons, indicate whether each of the following statements is true or false.

a) Ga-67 would be produced at 5-fold higher yields.

b) Ga-67 would be produced at 5-fold lower yields.

c) Ga-67 would be produced at lower yields, and contamination by Cu-64, Co-55, Co-57 would increase.

d) Ga-67 would be produced at lower yields, and contamination by Cu-64, Co-55, Co-57 would remain the same.

Theoretical Problem 3.
Stereochemistry

Dodecahedrane $C_{20}H_{20}$ is a polyhedron made of 12 regular pentagons and no double bonds. Ovalene $C_{32}H_{14}$ is a planar conjugated structure made of 10 regular hexagons which can be described as one naphthacene fused between two anthracenes.

3-1. What are the CCC angles for each of these rings?

3-2. Which configuration (trigonal planar, 120°; tetrahedral 109.5°; octahedral 90°) do the above CCC angles most closely match?

3-3. What is the hybridization which most closely conforms to the geometric structure of dodecahedrane and of ovalene?

A 'juncture' is defined here to mean any 3-ring system, sharing a common central atom, within a molecule. Compare the junctures within dodecahedrane and within ovalene. Consider an axis passing through the central C-atom of each juncture such that the angles the axes form with all three C–C bonds radiating from this C-atom are identical.

3-4. What is the value of this angle for dodecahedrane (to the nearest three degrees) and for ovalene?

3-5. Substracting 90° from each of the above angles describes the deviation from planarity for each juncture. Which juncture is planar?
Now consider dodecahedrene $C_{20}H_{18}$

which is dodecahedrane with one double bond between two consecutive C-atoms, and compare with ovalene.

3-6. For which C=C bond is H_2 addition expected more exothermic?

And now, on to fullerenes. For all known fullerenes, the deviation from planarity at any juncture is less than as is the case for dodecahedrane. For C_{60}, all junctures are equivalent. Now consider H_2 addition at a C=C bond of C_{60}.

3-7. For which of C_{60}, dodecahedrene, or ovalene is H_2 addition most exothermic?

3-8. For which of C_{60}, dodecahedrene, or ovalene is H_2 addition least exothermic?

Suppose A is the juncture between two hexagons and one pentagon, B the juncture between three hexagons, and C the juncture between two pentagons and one hexagon.

3-9. Which juncture has the least deviation from planarity?

3-10. Which junction has the greatest deviation from planarity?

Finally consider the larger fullerene C_{180}. To a first approximation, both C_{60} and C_{180} are perfect spheres.

3-11. Which has the larger deviation from planarity at each junction ? C_{60} or C_{180}?

3-12. Compare the relative enthalpies of formation, in kJ g^{-1} units, of C_{60}, C_{180}, and graphite.

Theoretical Problem 5.
Chemistry of Gold

Metallic gold can be extracted from gold mines by treating the crushed rock with aerated sodium-cyanide solution. During this process, gold is slowly converted to $[Au(CN)_2]^-$ which is soluble in water (reaction 1). The aq. soln. is then pumped off, and the metallic gold is recovered from it by reacting the gold complex with zinc which is converted to $[Zn(CN)_4]^{2-}$ (reaction 2).

5-1. Write ionic equations for reactions 1 and 2.

Gold in nature is frequently alloyed with silver which is also oxidized by aerated NaCN solution

5-2. 500 l of a soln. 0.0100M in $[Au(CN)_2]^-$ and 0.0030M $[Ag(CN)_2]^-$ was evaporated to one third of its original volume and was treated with 40 g of zinc. Calculate the concentrations of $[Au(CN)_2]^-$ and of $[Ag(CN)_2]^-$ after the reaction has ceased.
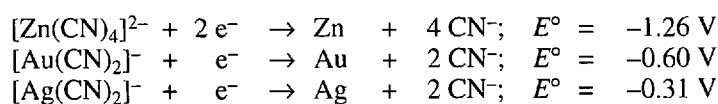
5-3. $[Au(CN)_2]^-$ is a very stable complex under certain conditions. $K_f([Au(CN)_2]^-) = 4 \cdot 10^{28}$. What concentration of cyanide ion is required to keep 99 mol% of the gold in solution in the form of the cyanide complex?

5-4. There has been several efforts to develop gold extraction processes which could replace this one. Is it due to

a) corrosion due to cyanide solutions on mining machinery?

b) toxicity problems?

c) quality of the gold obtained?

Theoretical Problem 6.
Mass Spectrometry and NMR

Unlike carbon, tin can increase its coordination number beyond 4. Like carbon, tin forms a chloride $SnCl_4$.

6-1. Draw two alternative geometries for $SnCl_4$.

Lewis acids such as $SnCl_4$ react with *Lewis* bases such as chlorides, and the following two reactions are observed:

$SnCl_4 + Cl^- \rightarrow SnCl_5^-$
$SnCl_4 + 2 Cl^- \rightarrow SnCl_6^{2-}$
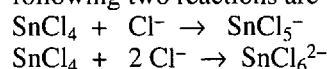
6-1. Draw alternative geometries for $SnCl_5^-$ and $SnCl_6^{2-}$.

6-2. Use Valence Shell Electron Pair Repulsion (VSEPR) theory to predict which geometry is likely to be preferred for $SnCl_5^-$ and $SnCl_6^{2-}$.

A soln. containing $SnCl_6^{2-}$ (as tetrabutylammonium salt) was examined by negative-ion electrospray mass spectrometry (ESMS). The spectrum contains a single peak at $m/z = 295$, if it is assumed that the only isotopes observed are ^{120}Sn and ^{35}Cl.

6-3. Write the empirical formula for the tin-containing species detected by this technique.

A soln. containing $SnBr_6^{2-}$ (as tetrabutylammonium salt) was examined by the same ESMS technique. The spectrum contains a single peak at $m/z = 515$, if it is assumed that the only isotopes observed are ^{120}Sn and ^{79}Br.

6-4. Write the empirical formula for the tin-containing species detected by this technique.

The ESMS spectrum of a soln. made by mixing equimolar amounts of $SnCl_6^{2-}$ and $SnBr_6^{2-}$ (as tetrabutylammonium salt) shows six major species at $m/z = 295, 339, 383, 427, 471,$ and 515.

6-5. Write the formula for each of the four new species.

^1H- and ^{13}C-NMR spectroscopy of molecules enable detection of a separate signal for each ^1H and ^{13}C nucleus which is in a different environment. These signals are recorded on a dimensionless ppm scale relative to some agreed standard reference compound. Similarly, ^{119}Sn gives a signal for each tin atom which is in a different environment.

The ^{119}Sn-NMR spectrum of a soln. of $SnCl_6^{2-}$ (as tetrabutylammonium salt) contains only one signal which occurs at −732 ppm relative to tetramethyltin Me_4Sn. This peak occurs at −2064 ppm if the soln. contains $SnBr_6^{2-}$ instead. But if the soln. contains equimolar amounts of $SnCl_6^{2-}$ and $SnBr_6^{2-}$, the spectrum contains seven peaks, with five new peaks at −912 ppm, −1117 ppm, −1322 ppm, −1554 ppm, and −1800 ppm.

6-6. Write the empirical formula for each of the tin-containing species in the mixture that gives rise to the five new peaks.

Cooling the soln. to −30° causes a change to this ^{119}Sn-NMR spectrum. New peaks are observed at −1092 ppm and −1336 ppm.

6-7. Draw the geometry for each of the four tin-containing species present at −30° that gives rise to the peaks at −1092 and −1117, −1322 and −1336 ppm.

Theoretical Problem 7.
Organic Synthesis

The fungus *Aspergillus nidullans* produces two isomeric aromatic lactones (cyclic esters) A and B ($C_{10}H_{10}O_4$), each of which dissolved in cold aq. NaOH soln. but not in aq. $NaHCO_3$. Both A and B give a violet color with aq. $FeCl_3$. Reaction of A with CH_3I in the presence of K_2CO_3 gives C ($C_{11}H_{12}O_4$) which was shown by NMR to contain three non-identical methyl groups, one of which was bound directly to the aromatic ring. Selective demethylation of C with BCl_3 followed by aq. workup gave D, a new isomer of A. The NMR spectrum of D showed the presence of an intramolecular hydrogen-bonded hydroxy group at $\delta = 11.8$ ppm. Compound D was synthesized as follows.
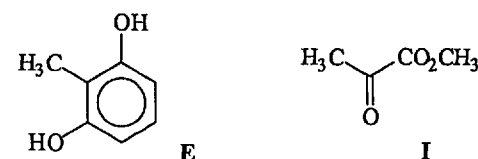
The phenol E was methylated (MeI/ K_2CO_3) to afford F ($C_9H_{12}O_2$) which in turn was reduced with lithium metal in liquid ammonia and 2-methylpropan-2-ol to give the symmetrical unconjugated diene G. Conjugation of this diene was

$[Zn(CN)_4]^{2-} + 2 e^- \rightarrow Zn + 4 CN^-;\quad E° = -1.26 V$
$[Au(CN)_2]^- + e^- \rightarrow Au + 2 CN^-;\quad E° = -0.60 V$
$[Ag(CN)_2]^- + e^- \rightarrow Ag + 2 CN^-;\quad E° = -0.31 V$

achieved by reaction with KNH_2 in liquid ammonia followed by aq. workup, a process which afforded only one product **H**. Ozonolysis of **H** followed by non-reductive workup afforded amongst other products the keto ester **I**. Compound **H** underwent a *Diels-Alder* reaction with dimethyl but-2-ynedioate **J** to give the adduct **K** ($C_{15}H_{20}O_6$) which upon heating expelled ethene to afford an aromatic ester **L**. Basic hydrolysis of **L** followed by acidification of the soln. gave **M** ($C_{11}H_{12}O_6$) which when heated under vacuum yielded **N** ($C_{11}H_{10}O_5$). Reduction of **N** with $NaBH_4$ in dimethylformamide gave **C** and an isomeric lactone **O** which could also be obtained by the methylation of **B**.

7-1. What are the structures **A** to **O**?

7-2. Provide a second structure **P** for **B**.

Practical Problem 1

Determination of calcium by precipitation with oxalate followed by titration with permanganate.

Practical Problem 2

Analysis of a mixture of $[Co(NH_3)_5\text{-}NO_2]Cl_2$ + $[Co(NH_3)_6]Cl_3$ using a cation-exchange resin RSO_3H and titration by $0.01M$ NaOH.

Answers

1-1. $PbCl_2$

1-2. $PbCl_2 + H_2Y^{2-} \rightarrow PbY^{2-} + 2 H^+ + 2 Cl^-$

1-3. pH buffer

1-4. Metallochromic indicator

1-5. *i*). $Pb^{2+} + H_2Y^{2-} \rightarrow PbY^{2-} + 2 H^+$
 ii). $PbH_2Y^{2-} + XO$ (yellow) $\rightarrow$ $PbXO^{2+}$ (red)

1-6. NaF complexes Sn

1-7. $SnY + 6 F^- + 2 H^+ \rightarrow SnF_6^{2-} + H_2Y^{2-}$

1-8. $H_2Y^{2-} + PbXO^{2+} \rightarrow PbY^{2-} + XO$ (yellow) $+ H^+$

1-9. 43.7% Sn; 56.4% Pb

2-1. 1819

2-2. Ra-226 – Rn-222

2-3. Use $0.2M$ HCl in 96% methanol to remove Ni-57, followed by $2M$ HCl in 55% propan-2-ol to remove Co-55, followed by $1M$ HCl in 55% propan-2-ol to remove Cu-64.

2-4. *b,c* true; *a,d,e* false

2-5. *a,b,c* true; *d* false

2-6. *b,d* true; *a,c* false

3-1. Dodecahedrane 108°; Ovalene 120°

3-2. Ovalene is trigonal planar. Dodecahedrane is tetrahedral.

3-3. Ovalene sp^2. Dodecahedrane sp^3

3-4. Dodecahedrane 109–115°. Ovalene 90°

3-5. Ovalene

3-6. Dodecahedrene

3-7. Dodecahedrene

3-8. Ovalene

3-9. B

3-10. C

3-11. C_{60}

3-12. $\Delta H°_f(C_{60}) > \Delta H°_f(C_{180}) > \Delta H°_f(\text{graphite})$

5-1.1. $4 Au + 8 CN^- + O_2 + 2 H_2O \rightarrow 4 [Au(CN)_2]^- + 4 OH^-$

5-1.2. $Zn + 2 [Au(CN)_2]^- \rightarrow [Zn(CN)_4]^{2-} + 2 Au$

5-2. $[Au(CN)_2]^- = 0.030M$; $[Ag(CN)_2]^- = 0.002M$

5-3. $[CN^-] = 5 \cdot 10^{14}$

5-4. *b*

6-1. Many possibilities

6-2. Double triangular pyramid and octahedron

6-3. $SnCl_5^-$

6-4. $SnBr_5^-$

6-5. $SnCl_4Br^-$, $SnCl_3Br_2^-$, $SnCl_2Br_3^-$, $SnClBr_4^-$

6-6. $SnCl_5Br^{2-}$, $SnCl_4Br_2^{2-}$, $SnCl_3Br_3^{2-}$, $SnCl_2Br_4^{2-}$, $SnClBr_5^{2-}$

6-7. Near -1110 ppm, the peaks are *cis*- and *trans*-isomers. Near -1330 ppm, the peaks are caused by *fac*- and *mer*-isomers.

7-1 + 7-2.