Name: Code: XXX-

Task 1 10% of the total

1a	1b	1c	1d	Task 1
30	2	12	4	48

a) Yield of the product in g, measured by the organizer:

The samples are dried by the organisers. Full pts for a 60-100% yield, linear scale between 0-60% yield. The typical yield is 70%.
Purity is checked by solubility (acetone) and TLC. If there is no insoluble material and no impurity is detectable by TLC, the full points for the yield are received.
If there is a considerable (easily visible) amount of insoluble material or impurity on the TLC plate, then 0 point is received for the yield (only possible in case of intentional contamination).
5 points off if filter disc is submitted.

b) Calculate the theoretical yield of your product in g.

$C_6H_{12}O_6 \rightarrow C_{16}H_{22}O_{11}$

$$m = \frac{3.00\,g \cdot 390\,g/mol}{180\,g/mol} = 6.5\ g$$

Theoretical yield:

c) Sketch your developed TLC plate and leave on your desk to be evaluated,

If both standards and all samples are present and labeled: 5 pts
If any sample is missing: 2 pts, if more than one is missing: 0 pt.
Loading of the plate: if over- or underloading does not interfere with the evaluability: 4 pts, if interfering, but evaluation is still possible: 2 pts, if evaluation is not possible: 0 pt
If the development is appropriate (minor tilting is acceptable): 3 pts. If erratically developed, but still evaluable (the two isomers separate): 1 pt, otherwise 0 pt.

d) **Interpret your experiment** and choose the correct answer.

The acetylation reaction of glucose is exothermic.

- ☐ a) Yes
- ☐ b) No
- ☐ c) Cannot be decided based on these experiments

The isomerisation reaction of β-D-glucopyranose pentaacetate can be used for the preparation of pure α-D-glucopyranose pentaacetate.

- ☐ a) Yes
- ☐ b) No
- ☐ c) Cannot be decided based on these experiments

Solutions: a, a (2 pts. each)

Name: Code: XXX-

Task 2 15 % of the total

2a	2b	2c	2d	2e	Task 2
25	4	25	6	5	65

a) Ce^{4+} consumptions:

Full marks (25 pts.) if V_1 is within 0.15 cm^3 of the expected value recalculated from the $K_4[Fe(CN)_6]$ mass. Zero marks if deviation is more than 0.50 cm^3. Linear scale is applied in between.

Average volume consumed (V_1):

b) The titration reaction:

$Ce^{4+} + [Fe(CN)_6]^{4-} = Ce^{3+} + [Fe(CN)_6]^{3-}$ 2 pts.

or

$Ce^{4+} + Fe^{2+} = Ce^{3+} + Fe^{3+}$ 1 pt.

Calculation of sample mass:

$m = c_{Ce} V_1 10 \cdot M$ 2 pts.

Actual sample masses will be distributed with the exam copies.

$K_4[Fe(CN)_6].3H_2O$ mass (m):

c) Zinc consumptions:

Full marks (25 pts.) if V_2 is within 0.15 cm^3 of the expected value recalculated from $K_4[Fe(CN)_6]$ mass, zinc concentrations and empirical ratio. Zero marks if the deviation is more than 0.50 cm^3. Linear scale is applied in between.

Average volume consumed (V_2):

d) Mark the correct answer.

The diphenyl amine indicator changes in colour at the end point

- ☐ a) because the concentration of the Zn^{2+} ions increases.
- ☐ b) because the concentration of the $[Fe(CN)_6]^{4-}$ ions decreases.
- ☐ c) because the concentration of the $[Fe(CN)_6]^{3-}$ ions increases.
- ☐ d) because the indicator is liberated from its complex.

Which form of the indicator is present before the end point?

- ☐ a) Oxidized
- ☐ b) Reduced
- ☐ c) Complexed to a metal ion

At the beginning of the titration the redox potential for the hexacyanoferrate(II) - hexacyanoferrate(III) system is lower than the redox potential of the diphenyl amine indicator.

- ☐ a) True
- ☐ b) False

Solutions: b, b, a (2 pts. each)

e) Determine the formula of the precipitate. Show your work.

The mole ratio of the zinc:hexacyanoferrate(II) in the precipitate can be evaluated as:

$$n_{Zn}/n_{Fe(CN)_6} = \frac{10c_{Zn}V_2M}{m}$$

Values for c_{Zn} are distributed according to country color (found on seating plan)

Red/Pink: 0.0500 Green: 0.0450 Blue: 0.0475 Yellow/Ivory: 0.0525

The empirical ratio obtained from the experiments is 1.489.

Calculating the zinc/hexacyanoferrate(II) ratio: 3 pts.

Cations are needed to make the precipitate neutral and only potassium is present.

The precipitate is $K_2Zn_3[Fe(CN)_6]_2$. 2 pts.

Any other reasonable calculation giving the same result is accepted.

Hydrogen instead of potassium ($H_2Zn_3[Fe(CN)_6]_2$ or $KHZn_3[Fe(CN)_6]_2$) is also acceptable.

Mistakes in units, dilution factors, significant figures (not 3 or 4 in 2b) carry a penalty of 1 pt. in each calculation.

The formula of the precipitate:

Items replaced or refilled: Student signature: Supervisor signature:

Name: Code: XXX-

Task 3 15 % of the total

Task 3
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Only fill out this table when you are ready with all your assignments.

	1	2	3	4	5	6	7	8
Cation								
Anion								

6 pts for each correctly identified ion except for HCO_3^- and HS^- which are worth 12 pts, bringing up the total to 108 points.

Partial points will be awarded in the following cases:

Anions:
$AgNO_3$: Full points if NO_3^- is the only anion shown. 3 pts for ClO_4^- only. 3 pts if fluoride appears together with nitrate and/or perchlorate. Otherwise 0 pt.
$Pb(CH_3COO)_2$: 3 pts if NO_3^- and/or ClO_4^- appear together with CH_3COO^-. 1 pt for nitrate and/or perchlorate on their own. Otherwise 0 pt.
3 pts for CO_3^{2-} instead of HCO_3^-, and for S^{2-} instead of HS^-.

Cations:
In the case of all alkali metal compounds, 2 pts for an incorrect alkali metal.
1 pt for Ca^{2+} or Sr^{2+} instead of Ba^{2+}.

Solution

The solutions received by the students contain the following compounds. The country colours can be found on the laboratory seating plan.

Country colour	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**
Blue	$AgNO_3$	$KHCO_3$	NH_4ClO_4	NaOH	NaHS	$Pb(OAc)_2$	BaI_2	$MgSO_4$
Green	$Pb(OAc)_2$	NH_4ClO_4	NaOH	NaHS	$MgSO_4$	$KHCO_3$	$AgNO_3$	BaI_2
Ivory	NH_4ClO_4	$Pb(OAc)_2$	$KHCO_3$	BaI_2	$AgNO_3$	$MgSO_4$	NaHS	NaOH
L.Blue	NaHS	$MgSO_4$	BaI_2	NH_4ClO_4	$Pb(OAc)_2$	$AgNO_3$	NaOH	$KHCO_3$
L.Green	BaI_2	NaHS	$MgSO_4$	$AgNO_3$	NaOH	NH_4ClO_4	$KHCO_3$	$Pb(OAc)_2$
Pink	$MgSO_4$	NaOH	$AgNO_3$	$Pb(OAc)_2$	$KHCO_3$	BaI_2	NH_4ClO_4	NaHS
Red	NaOH	BaI_2	$Pb(OAc)_2$	$KHCO_3$	NH_4ClO_4	NaHS	$MgSO_4$	$AgNO_3$
Yellow	$KHCO_3$	$AgNO_3$	NaHS	$MgSO_4$	BaI_2	NaOH	$Pb(OAc)_2$	NH_4ClO_4

The problem can be approached in many ways. Intuition is very helpful in the tentative assignment of some compounds in the early phases of the work. A systematic solution is given here for the blue Country colour.

All solutions are colourless (NaHS may be slightly yellowish because of polysulfide impurity). Solutions **1**, **3**, **6**, **7**, and **8** are practically neutral (pH paper reading about 5-6). Solution **2** is basic (pH = 9) while solutions **4** and **5** are very strongly basic (pH > 11).

We can exclude all ions that only form coloured compounds in aqueous solutions: Cr^{3+}, Fe^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and $MnO_4^–$. (In principle we should also exclude Mn^{2+} but its solutions have a very light pink colour that might be mistaken for colourless. The yellowish solution is strongly basic hence its colour cannot be attributed to iron.) The compounds of H^+, Sn^{2+}, Sn^{4+}, Sb^{3+}, Bi^{3+}, and $HSO_4^–$ with the possible counter-ions could only exist in markedly acidic solutions; therefore they can also be safely excluded.

Thus the list of possible ions is:

Cations: NH_4^+, Li^+, Na^+, Mg^{2+}, Al^{3+}, K^+, Ca^{2+}, Mn^{2+}, Zn^{2+}, Sr^{2+}, Ag^+, Ba^{2+}, Pb^{2+}.

Anions: $OH^–$, $CO_3^{2–}$, $HCO_3^–$, $CH_3COO^–$, $C_2O_4^{2–}$, $NO_2^–$, $NO_3^–$, $F^–$, $PO_4^{3–}$, $HPO_4^{2–}$, $H_2PO_4^–$, $SO_4^{2–}$, $S^{2–}$, $HS^–$, $Cl^–$, $ClO_4^–$, $Br^–$, $I^–$.

The unknown solutions react with each other as follows (↓ = precipitate; ↑ = volatile product; "no change" means even when boiled, unless indicated otherwise):

	1 $AgNO_3$	**2** $KHCO_3$	**3** NH_4ClO_4	**4** $NaOH$	**5** $NaHS$	**6** $Pb(OAc)_2$	**7** BaI_2	**8** $MgSO_4$
1 $AgNO_3$	—	—	—	—	—	—	—	—
2 $KHCO_3$	↓ light yellow ↑ neutral, odourless	—	—	—	—	—	—	—
3 NH_4ClO_4	no change	↓ white crystals (*)	—	—	—	—	—	—
4 $NaOH$	↓ brown-black	no change	boiling: ↑ basic, odour of ammonia	—	—	—	—	—
5 $NaHS$	↓ black solution turns acidic	no change	boiling: ↑ basic, odour of NH_3, H_2S	no change	—	—	—	—
6 $Pb(OAc)_2$	↓ white crystals	↓ white ↑ neutral, odourless	no change	↓ white	↓ black	—	—	—
7 BaI_2	↓ yellow	↓ white ↑ (**)	no change	no change	no change	↓ yellow	—	—
8 $MgSO_4$	↓ white crystals	no change (***)	no change	↓ white	no change (****)	↓ white	↓ white	—

(*): upon boiling, the formation of NH_3 is detectable by its odour and by pH paper.
(**): gas bubbles are usually not observed when **2** is in excess.
(***): upon boiling, an odourless gas evolves and a white precipitate forms.
(****): upon boiling, a white precipitate forms and the odour of H_2S appears.

$2\ Ag^+ + 2\ HCO_3^- = Ag_2CO_3 + CO_2 + H_2O$

$Pb^{2+} + 2\ HCO_3^- = PbCO_3 + CO_2 + H_2O$

$Ba^{2+} + 2\ HCO_3^- = BaCO_3 + CO_2 + H_2O$

$Mg^{2+} + 2\ HCO_3^- = MgCO_3 + CO_2 + H_2O$ (more accurately, basic carbonates of variable composition are formed)

$Ag^+ + I^- = AgI$; $2\ Ag^+ + SO_4^{2-} = Ag_2SO_4$; $Ag^+ + CH_3COO^- = CH_3COOAg$

$Pb^{2+} + 2\ OH^- = Pb(OH)_2$; $Pb^{2+} + 2\ I^- = PbI_2$; $Pb^{2+} + SO_4^{2-} = PbSO_4$

$K^+ + ClO_4^- = KClO_4$; $Ba^{2+} + SO_4^{2-} = BaSO_4$; $Mg^{2+} + 2\ OH^- = Mg(OH)_2$

$2\ Ag^+ + 2\ OH^- = Ag_2O + H_2O$

$2\ Ag^+ + HS^- = Ag_2S + H^+$; $Pb^{2+} + HS^- = PbS + H^+$; $CH_3COO^- + H^+ = CH_3COOH$

$NH_4^+ + OH^- = NH_3 + H_2O$

$NH_4^+ + HCO_3^- = NH_3 + CO_2 + H_2O$

Two groups of the observed phenomena give instant clues to the identification of some of the ions.

First, the reactions of **2** are often accompanied with the formation of a colourless and odourless gas that can only be CO_2.Thus **2** contains CO_3^{2-} or HCO_3^-.

Second, there are only 3 dark precipitates that can form from the given ions: Ag_2O, Ag_2S, and PbS. This fact, together with the pH of the solutions, instantly identifies the cation of **1** as $\mathbf{Ag^+}$, the cation of **6** as $\mathbf{Pb^{2+}}$, the anion of **4** as $\mathbf{OH^-}$, and the anion of **5** as sulfide or hydrosulfide (confirmed by the distinct smell of the solution).

The choice between the latter two can be made by measuring the pH of the solution formed in the reaction of **5** with an excess of **1** or **6**. In the case of **1**, the reaction mixture is strongly acidic. Thus the anion of **5** is $\mathbf{HS^-}$.

The evolution of CO_2 in the reaction with Ag^+ and Pb^{2+} also identifies the anion of **2** as $\mathbf{HCO_3^-}$. (in accord with the moderately basic pH)

The reaction of **3** and **4** yields ammonia. **4** is obviously not a solution of NH_3 itself. Thus the cation of **3** is $\mathbf{NH_4^+}$.

2+**4** do not form either a precipitate or ammonia. The cations of **2** and **4** are Na^+ or K^+.

2+**5** do not form either a precipitate or ammonia. The cation of **5** is an alkali metal.

3 is the only solution that does not give a precipitate with Ag^+. Accordingly, it can be ammonium nitrate, fluoride, or perchlorate. But it does give a precipitate with **2**, a hydrocarbonate of Na^+ or K^+. Thus the anion of **3** is $\mathbf{ClO_4^-}$ and the cation of **2** is $\mathbf{K^+}$.

4 does not give a precipitate with NH_4ClO_4. The cation of **4** is $\mathbf{Na^+}$.

5 does not give a precipitate either with NH_4ClO_4 (K^+) or with a mixture of $KHCO_3$ and NaOH (Li^+). The cation of **5** is $\mathbf{Na^+}$.

7 forms no precipitate or ammonia with NaOH but gives a precipitate with $KHCO_3$. **7** cannot be an alkali metal perchlorate because it forms yellow precipitates with **1** and **6**. Thus the cation of **7** is $\mathbf{Ba^{2+}}$ and the anion of **7** is $\mathbf{I^-}$.

At room temperature **8** gives a precipitate with OH^- but not with HS^- which means it can only be a salt of a Group 2A metal. Thus the reaction of **8** with BaI_2 is obviously one between Ba^{2+} and the anion of **8**. The latter is very likely SO_4^{2-} but HCO_3^- and $H_2PO_4^-$ are also theoretically possible. The solution of **8** is unchanged upon boiling and gives a white precipitate with Ag^+. This excludes both HCO_3^- and $H_2PO_4^-$. Thus the anion of **8** is $\mathbf{SO_4^{2-}}$. This instantly identifies the cation of **8** as $\mathbf{Mg^{2+}}$.

6 is a soluble compound of lead. The anion could be CH_3COO^-, NO_2^-, NO_3^-, or ClO_4^-. The slight odour of acetic acid might give a clue. Unlike **1**, the reaction of an excess of **6** with HS^- does not yield a markedly acidic solution which shows that **6** is a salt of a weak acid. If **6** were a nitrite, it would give a yellowish precipitate with Ag^+. It would also react with NH_4ClO_4 upon heating with the evolution of N_2 (and nitrogen oxides from the reaction with HS^- would also be noticeable). The absence of these reactions indicates that the anion of **6** is $\mathbf{CH_3COO^-}$.

Soluble salts of silver are even less numerous, the only choices are NO_3^-, F^-, and ClO_4^-. The anion can be examined if one removes the silver ions from the solution of **1** with an excess of NaOH. The Ag_2O precipitate quickly separates from the solution which can be easily poured off. This solution, containing the anion of **1**, does not give a precipitate with BaI_2 which rules out F^-. The solubility of $KClO_4$ is quite significant; therefore the absence of a precipitate with $KHCO_3$ is inconclusive. The anion of **1** is therefore either $\mathbf{NO_3^-}$ or $\mathbf{ClO_4^-}$.